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THE PESTICIDE MANUFACTURING INDUSTRY-CURRENT WASTE TREATMENT AND DISPOSAL PRACTICES

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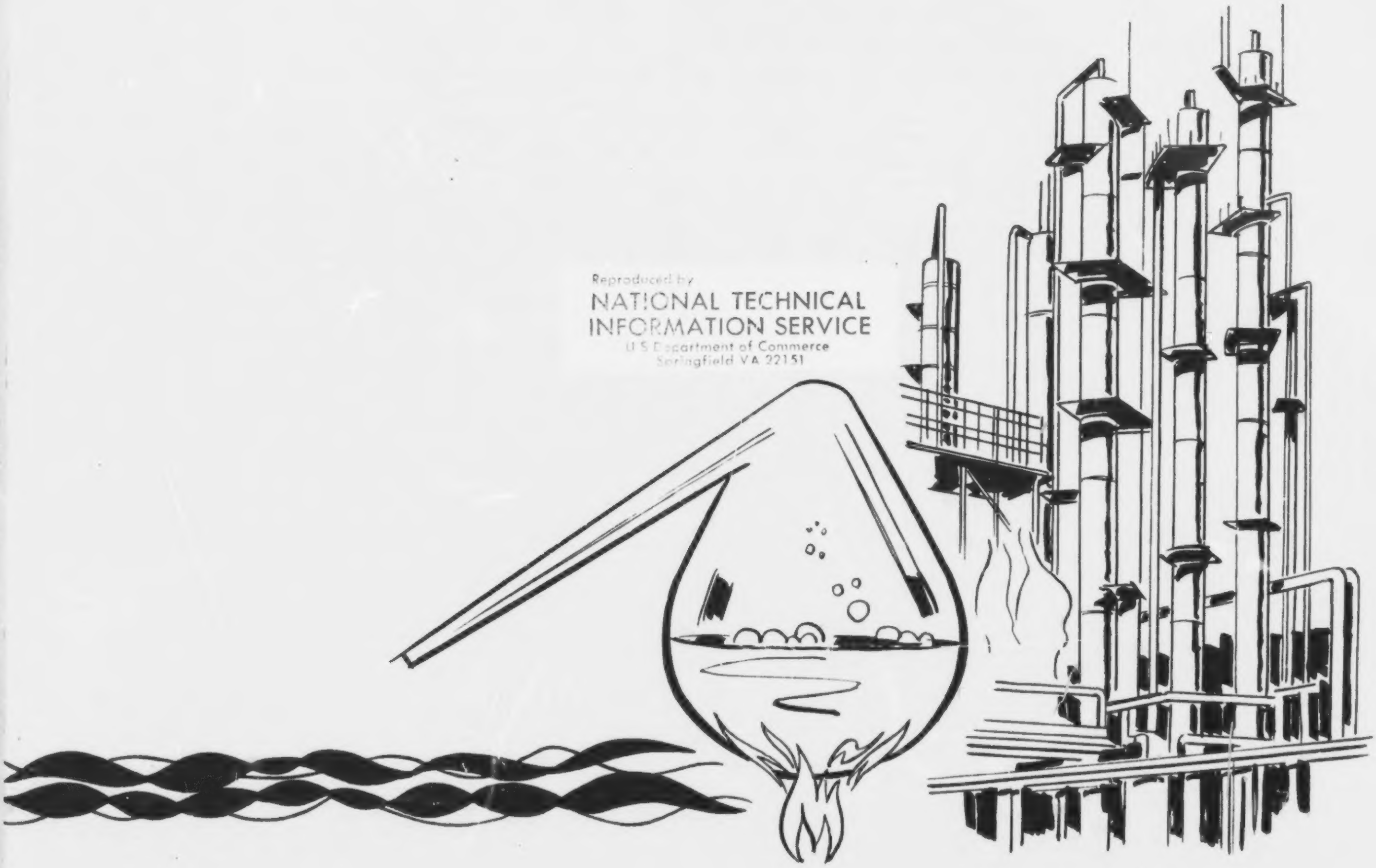

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16. Abstract An in-depth review of the literature, including government information documents, technical reports, the technical journals, industrial publications, and twenty plant interviews with plant managers and operators were used as the data base for studying the "state of the art" of pesticide manufacturing waste treatment and disposal practices. No attempts were made to prove or disprove statements made in the literature or statements made in the interviews. The report contains chapters dealing with: a) the present and projected pesticide demands in the United States, b) the chemistry of pesticides including production processes and waste generation, c) waste treatment possibilities discussed in the literature, d) pesticide waste treatment systems that have been or currently are in full scale operation, and e) the cost of pesticide waste treatment system. (Lowry-Texas)

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Abstractor Mark V. Lowry

Institution Texas Univ, Austin

THE PESTICIDE MANUFACTURING INDUSTRY - CURRENT WASTE TREATMENT AND DISPOSAL PRACTICES

OK

by

Patrick R. Atkins
The University of Texas
Austin, Texas 78712

for the

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ABSTRACT

Numerous pesticides and pesticide manufacturing processes are in use in the United States. The wastes produced are varied and possess characteristics which make them unique. This study was undertaken to determine the State of the Art of the waste treatment practices utilized by the industry to manage these wastes. A literature search was conducted and the data obtained was supplemented with interviews conducted at twenty pesticide manufacturing plants.

Since pesticide manufacture is an extremely sensitive area at the present time, much of the information obtained is incomplete. However, the data presented should be of considerable use to those planning waste treatment facilities. The report contains information on current and predicted pesticide production trends, a description of typical pesticide manufacturing processes, a review of the literature which describes pesticide chemistry and waste treatment practices, a detailed summary of the waste treatment systems discussed in the plant interviews, and cost estimates.

The report is designed to be a basic reference document containing information on the spectrum of treatment and disposal methods in current use. No attempt was made to prove or disprove statements made in the literature or the plant interviews. Areas of needed research are discussed in the recommendations section.

CONTENTS

Chapter		Page
I	Conclusions	1
II	Recommendations	9
III	Pesticide Production and Use	15
	Definition of Pesticides	15
	Trends in Production and Use	15
	Recent Production and Sales Data	17
	Forecasts in Production and Use	26
IV	Pesticide Manufacture	31
	Producers of Pesticides	31
	Manufacturing Processes and Waste Generation	31
	DDT	32
	Carbaryl	33
	Parathion and Methyl Parathion	34
	2,4,5-T, 2,4-D and MCPA Herbicides	35
	Diolefin-based Insecticides	36
V	Pesticidal Waste Treatment Techniques: Removal, Detoxification, Degradation and Decomposition	41
	Chemistry of Pesticides	41
	Natural Insecticides	41
	Carbamates	41
	Organophosphorus Insecticides	41
	Chlorinated Hydrocarbons	42
	Treatment Methods	44
	Chemical Oxidation	44
	Coagulation	52
	Adsorption	55
	Photochemical Degradation	70
	Liquid-Liquid Extraction	70
	Biological Degradation	74
	Foam Fractionation	85
	Disposal Methods	85
	Combustion	85
	Burial	89

CONTENTS (Continued)

Chapter		Page
	Ocean Dumping	93
	Deep Well Disposal	95
VI	Treatment and Disposal Practices Presently Employed	99
	In-Plant Control	99
	Neutralization and pH Adjustment	100
	Chemical Treatment	101
	Physical Treatment	108
	Biological Treatment	113
	Basic Requirements	114
	Temperature	114
	pH	114
	Nutrients	119
	Degradability	119
	Trickling Filters	121
	Activated Sludge	122
	Aerated Lagoon	125
	Stabilization Ponds	126
	Incineration	127
	Burial	134
VII	The Cost of Waste Treatment	137
	Photochemical Degradation	137
	Activated Carbon	138
	Chemical Treatment	139
	Biological Treatment	139
	Incineration	147
	Burial	148
	Ocean Disposal	150
VIII	Acknowledgments	153
IX	References	155
X	Appendices	163

FIGURES

Page

1 Classification and Relative Importance of Pesticides (Anon., Chem. Engr., 1969) 16

2 Past and Projected Pesticide Production in the U.S. (Neumeyer, *et al*., 1969) 27

3 Oxidation of 2,4-DCP with Potassium Permanganate (Aly and Faust, 1965) 46

4 Removal of Lindane by Treatment with Potassium Permanganate (Buescher, *et al*., 1964) 47

5 Removal of Lindane by Aeration and Ozonation (Buescher, *et al*., 1964) 48

6 Removal of Aldrin by Aeration and Ozonation (Buescher, *et al*., 1964) 49

7 Removal of Dieldrin by Aeration and Ozonation (Buescher, *et al*., 1964) 50

8 Effectiveness of Chlorine Treatment of 0.1 mg/l Rotenone Solution (Cohen, *et al*., 1960) 53

9 Contact Time and Chlorine Dioxide Required to Detoxify 0.1 mg/l Rotenone (Cohen, *et al*., 1960) 54

10 Carbon Dosage Curves for Removal of Fish Poisons (Cohen, *et al*., 1960) 62

11 Removal of DDT from Solution as a Function of Contact Time (Whitehouse, 1967) 63

12 Removal of Aldrin from Solution as a Function of Contact Time (Whitehouse, 1967) 64

FIGURES (Continued) Page

13 Removal of Dieldrin from Solution as a Function of Contact Time (Whitehouse, 1967) 65

14 Removal of Dieldrin from Solution as a Function of Carbon Dosage (Whitehouse, 1967) 66

15 Removal of Aldrin from Solution as a Function of Carbon Dosage (Whitehouse, 1967) 67

16 Removal of DDT from Solution as a Function of Carbon Dosage (Whitehouse, 1967) 68

17 Photochemical Degradation Rates for Aldrin, Dieldrin, and Endrin (2537 Å source) (Bulla and Edgerly, 1968) 71

18 Dilution Effect on Respiration Rates (Ford and Gloyna, 1967 76

19 Batch Aeration of 2,4-D & 2,4,5-T Acid Wastes (Ford and Gloyna, 1967) 77

20 Anaerobic Degradation of Lindane in Sludge Containing 1.5% Dry Solids at 35°C (Hill and McCarty, 1969) 79

21 Anaerobic Degradation of Lindane in Active and Poisoned Sludge at 35°C (Hill and McCarty, 1967) 80

22 Anaerobic Degradation of Single Pesticides in 3500 ml of 7.2% Total Solids Sludge at 35°C (Hill and Mccarty, 1967) 81

23 Anaerobic Degradation of Pesticide Mixtures in Thick Sludge at 35°C (pesticides without extractable degradation products) (Hill and McCarty, 1967) 82

24 Anaerobic Degradation of Pesticide Mixtures in Thick Sludge at 35°C (pesticides with extractable degradation products) (Hill and McCarty, 1967) 83

25 Pesticide Degradation in Dilute Sludge at 20°C (Hill and McCarty, 1967) 84

FIGURES (Continued) Page

26 Schematic Diagram of a Waste Injection Well Completed in Competent Sandstone (Warner, 1965) 97

27 Ozonation Test Results of Dehydrochlorination (DHC) Wastewaters (Ford and Eckenfelder, 1968) 107

28 The Effects of Temperature on BOD Removal from Soluble Industrial Wastes (Ford, 1971) 118

29 Capital Cost Relationship - Neutralization (Ford and Gloyna, 1970) 140

30 Capital Cost Relationship - Activated Sludge (Ford and Gloyna, 1970) 141

31 Capital Cost Relationship - Trickling Filters (EPA Report 12020 --- 2/70, 1970) 142

32 Capital Cost Relationship - Aerated Lagoon (EPA Report 12020 --- 2/70, 1970) 143

33 Capital Cost Relationship - Lagoons (EPA Report 12020 --- 2/70, 1970) 144

34 Capital Cost Relationship - Incineration (EPA Report 12020 --- 2/70, 1970) 149

35 The Cost of Solid Waste Disposal in Sanitary Landfills (Heaney, _et al_., 1970) 151

TABLES

No.		Page
1	Decrease in Inorganic Pesticide Usage in the U.S. (Anon., Chem. Engr., 1969)	17
2	Production Decline of Chlorinated Pesticides in U.S. (Anon., Chem. Engr., 1969)	18
3	U.S. Pesticide Production (Anon., Chem. Engr., 1969)	19
4	Synthetic Organic Pesticides: Volume and Value of Sales by Classes, U.S., 1966-1969 (Anon., U.S. Tariff Commission, 1969)	21
5	Pesticides and Related Products: U.S. Production and Sales (Anon., U.S. Tariff Commission, 1969)	23
6	Principal Products - Dominant Pesticide Products (Neumeyer, et al., 1969)	28
7	Waste Characteristics of Chlorinated Herbicide Wastes (Ford and Gloyna, 1967)	37
8	Effects of Oxidants on Pesticides in Aqueous Solution (Buescher, et al., 1964)	51
9	Summary of Cumulative Pesticide Removal at 10-ppb Load from Raw River Water (Robeck, et al., 1965)	57
10	Efficiency of Adsorption and Recovery from Carbon (Faust and Suffet, 1966)	58
11	Effect of Activated Carbon on Herbicides and Insecticides (Sigworth, 1965)	59
12	Carbon Dosages Required to Reduce the Concentration of 2,4-D Compounds (Aly and Faust, 1965)	61

No. Page

13 Carbon Dosages Required to Reduce the Concentration of 2,4-DCP (Aly and Faust, 1965) 61

14 Liquid-Liquid Extraction Systems and Percent Recoveries (Faust and Suffet, 1966) 72

15 Cumulative Pesticide Removed - Foam Foundation (Whitehouse, 1967) 86

16 Percent Loss on Combustion of Commercial Formulations of Pesticides at Five Temperatures (Kennedy, et al., 1969) 88

17 Relative Mobility of Pesticides in Soils (Working Group on Pesticides, 1970) 91

18 Chemical Treatment (Author, 1971) 103

19 Ozonation of Dehydrochlorination (DHC) Wastes (Ford and Eckenfelder, 1968) 106

20 Chemical Treatment (Anon., National Agr. Chemical Association, 1965) 109

21 Physical Treatment (Author, 1971) 110

22 Biological Treatment (Author, 1971) 115

23 Incineration (Author, 1971) 129

24 Costs for Various Degrees of Treatment for Different Combinations of Waste Characteristics (Barnard, 1970) 145

25 Estimated Marine Disposal Cost for 1968 (Witt, 1971) 152

CHAPTER I

CONCLUSIONS

Based on the information gathered during this study, the following conclusions have been formulated:

1. Pesticide usage in the United States will continue to grow in the future. The increasing demand for food and fiber and the spiraling cost of labor both act to insure the need for pesticides in the form of insecticides, fungicides and herbicides to make farm production more efficient. Legislation restricting the use of certain types of pesticides will have an impact on various phases of the pesticide industry, but in the main, pesticide production and use will continue to increase at the present rate or an accelerated rate.

2. Certain classes of pesticides may decrease in actual usage and will be replaced by other compounds which do not possess the characteristics which could make them potentially harmful to the environment. For example, long-lived DDT and related isomers will no doubt decrease in usage with a subsequent increase in the use of other broad spectrum pesticides from the organo-phosphate and carbamate classes.

3. As the total pesticide production and usage in the United States continues to grow, shifts in the use of certain classes of pesticides will be significant. The herbicide usage is increasing more rapidly than insecticide and fungicide usage and this trend will probably continue. Herbicides now occupy approximately 33.5% of the pesticide market and this percentage will increase as farm labor costs continue to spiral. The chlorinated hydrocarbon type herbicide usage has decreased but substitute compounds have more than made up for this decrease. The present projections of pesticide usage in the United States indicate an annual growth rate of approximately 16%. Herbicide usage is expected to increase at perhaps 20% per year. The use of alternate pest control methods including sterile insects, insect attractants, and insect traps may also effect the pesticide market. It is impossible at this time to predict the effect that these emerging techniques may have.

4. Because of the high cost of development, testing and marketing new pesticidal compounds (3-6 million dollars per product), few entirely new types of pesticides will probably be marketed in the near future. Even

though there is a trend toward shifting from the chlorinated hydrocarbon classes of pesticides, new substitute compounds will be few in number. Most of the replacement compounds will be existing pesticidal compounds or modifications of these existing compounds.

5. Many of the patents on major pesticides will expire within the next five years. This will open these compounds to the competitive market and will perhaps influence the price and usage rate of several major pesticidal compounds. Therefore, it is difficult to project the total pesticide usage and the percent of the market that will be occupied by the various types of pesticides beyond 5-10 years.

6. A large amount of information is available on the manufacturing processes involved in producing most pesticidal compounds. However, much of the success of a given reaction is based on a certain amount of "art" that cannot be described in the literature. These variations in production practices affect the quantity and quality of the waste streams resulting from the manufacturing process. For this reason, detailed data concerning wastewater characteristics, toxicity, treatability and volumes is almost impossible to obtain. Generalizations can be made and are included in this report. However, wide variations in wastewater quality can occur and these variations may require entirely different treatment systems for plants that are involved in producing the same type of basic compounds.

7. Wastewater streams from pesticide manufacturing generally contain total dissolved solids in excess of 10,000 mg/l, low suspended solids, high COD and some BOD, a small amount of toxic product and pH values that may range from very acid to highly basic. The wastes may resemble a number of typical industrial waste streams in many ways, but the presence of active pesticidal agents, solvents, high dissolved solids, and wide pH fluctuations pose unusual problems which must be considered when waste treatment and disposal systems are planned. Many of the treatment problems arise as a result of the high total dissolved solids or the wide pH fluctuations which can occur rather than from the organic components of the waste stream.

8. A large number of methods are being or have been used in treating pesticide manufacturing wastes. Much of the data is sketchy and incomplete. Since this is an area that receives wide-spread public attention, most manufacturers are hesitant to release information on any waste streams that contain pesticidal compounds, no matter how dilute the toxic

components may be. For this reason, much of the information on pesticide removal from waters arises from studies or processes designed to treat drinking water. Many of these processes appear to be applicable for handling waste treatment streams but others cannot be used for industrial wastes since the pesticidal wastes often contain extremely high dissolved solids, organic solvents, and acid or basic compounds.

9. Treatment methods including chemical oxidation with chlorine, chlorine dioxide, potassium permanganate, ozone and peroxide have been studied and shown to be capable of removing in excess of 95% of the active compounds from some types of pesticide manufacturing waste waters. Coagulation with alum and various polymers has been attempted with some success. Adsorption on activated carbon, saturated clays, humic acid, muck soils, bentonites, cation exchange resins, aluminum silicate and hydrous magnesium aluminum silicate have shown some promise as methods to remove small quantities of pesticides from aqueous systems. Photochemical degradation has also been successfully demonstrated as a method of treating waters containing small quantities of pesticidal compounds. Liquid-liquid extraction studies show that processes such as benzene extraction are effective in removing DDT from manufacturing wastes.

10. Biological degradation studies have been attempted by a large number of workers, but the unanswered questions concerning biological degradation of pesticidal wastes are still numerous and much work needs to be done in this area. Aerobic and anaerobic studies have been conducted under both laboratory, pilot and full-scale conditions. In many cases the biological system is quite effective in treating the pesticide waste. However, since the pesticide waste may be quite unique in characteristics, detailed laboratory studies or pilot studies should be conducted before any large-scale treatment system is designed and built. Aerobic and/or anaerobic organisms appear to be capable of degrading compounds such as 2,4-D, 2,4,5-T, malathion, parathion, lindane, heptachlor and silvex. Compounds such as dieldrin appear to be relatively bio-resistant, although some soil microbes have been reported to be active in degrading this particular pesticide.

11. Combustion is one of the most popular disposal methods for concentrated waste streams, semi-solids, and solid wastes. Many manufacturers indicate that the combustion process can effectively destroy most organic compounds (liquid and gaseous) but that problems arise because of other components in the wastes that are burned. The high salts may produce

feed system and burner maintenance problems, rapid corrosion and plume opacity; high burning temperatures produce oxides of nitrogen; sulfur and phosphorus compounds in the waste may be converted to sulfur dioxide and phosphorus pentoxide, which can cause downwind air pollution problems; compounds containing heavy metals such as lead, mercury and arsenic produce dangerous aerosols and require special precautions before incineration can be used safely.

12. Burial of pesticides is a common practice because of its relatively low cost. This method is practiced by almost all the pesticidal manufacturing operations that were visited during the course of this study. With the exception of one plant, no detailed studies were being conducted to determine the amount of horizontal or vertical movement of the materials buried at the landfill or pit disposal sites. The literature indicates that in general pesticide compounds move very little in a soil system. However, if the soil is not homogeneous or if groundwater intersects the burial zone, pesticidal migration is possible.

13. Ocean disposal is a convenient method of pesticide manufacturing waste disposal for manufacturing plants located near the oceans or the Gulf of Mexico. Concentrated liquid and semi-solid wastes are carried by barge in bulk form or in containers to dumping sites several miles to several hundred miles offshore. This type of system can be relatively inexpensive if conducted on a large scale. However, present regulatory authorities indicate that in the near future severe restrictions will be placed on this method of waste disposal. Therefore, long-term commitments to this type of disposal practice should be discouraged.

14. During this study a large number of pesticide manufacturing plants were visited and their waste treatment practices were discussed. The information obtained during these interviews is included in this report. The results of these interviews indicate that:

a. In-plant control of wastewater discharges entering the effluent stream can be an effective method of reducing the volume of wastewater and concentration of pollutants to be treated. Considerable interest in this method of water pollution abatement has been generated in the petrochemical industry. However, the belief is held by several operators that in the case of some pesticidal wastes, if large-scale reuse is employed, the resulting stream may be too concentrated to be amenable to treatment by many chemical and biological systems.

b. Continuous monitoring equipment on waste streams at several places in a plant has proven to be useful as a warning system to prevent toxic "slugs" from spills or upsets from reaching and possibly damaging chemical or biological treatment systems. A monitoring network plus diversion and storage facilities make it possible to contain and eventually treat these "slugs" rather than allowing them to pass through the system.

c. Neutralization and pH adjustment are necessary for most of the waste streams resulting from pesticide manufacturing. This neutralization may be needed for corrosion control, biological organism protection and receiving water protection. Limestone trenches, slaked lime feeders and neutralization basins are commonly used but many other chemical neutralization agents are employed as well. It has been found by at least one plant operator that a significant reduction in chemical costs (caustic) can occur if waste acids are mixed with the lighly basic wastes only after the low pH stream has been subjected to limestone trench treatment.

d. Several chemical treatment methods were in use to reduce wastewater problems at plants visited during this study. The chemical treatment methods varied widely in cost, application and effectiveness. The characteristics of the waste waters from pesticide manufacturing included such a broad spectrum of values that each chemical method had to be designed for the particular waste in question. Often these designs were made with little or no information on reaction rates, final reaction products, mixing requirements, etc.

e. Physical treatment methods in use at the various plants visited include carbon adsorption, sedimentation, filtration, heating, dilution and total evaporation. These types of treatment systems are very similar to those found in most petrochemical operations and differ very little from the standard design. However, extra care must be taken to reduce the probability of accidental spills and leakages because of the relatively high toxicity of some of the wastes.

f. Biological treatment systems are used extensively in treating pesticide manufacturing wastes. During this study several types of biological systems were in evidence, including trickling filters, activated sludge systems, aerated lagoons and stabilization ponds. BOD removals in the 80-95% range were reported for some trickling filter, activated sludge and aerated lagoon systems, and stabilization ponds achieved as much as 50% BOD reduction. Phenol and active pesticide removals were somewhat lower in most cases, but some systems including specially designed activated sludge systems achieved removals reported to be in excess of 99%. Most operators seem pleased with the biological units and the effluents produced. The high operating costs and the vulnerability of the systems to upsets were areas of major concern. Design criteria and operating parameters are included in the report if they were made available by the plant operators.

g. Several cities accept waste streams from petrochemical and pesticidal manufacturing plants, dilute these wastes with municipal sewage, and treat them in conventional municipal treatment systems. Oftentimes the pesticidal components in the industrial waste stream pass through the plant without complete degradation. Preliminary studies in the Delaware River Basin indicate that high concentrations of DDT and DDT degradation products have accumulated in sediments below outfalls from municipal treatment plants accepting industrial wastes. The effect of these compounds on the treatment plant itself is unknown and the effect on receiving waters and the benthal deposits in these receiving waters is yet to be determined.

h. Incineration practices in most of the plants visited indicate that a well-operated incinerator can be an extremely useful pesticidal waste disposal device. In no cases did any plant operator indicate that problems resulted from incomplete combustion of the pesticidal or organic components of the waste stream. Most problems appeared to be associated with the inorganic and corrosive components of the waste streams rather than the organic or pesticidal components. Particulate and gaseous pollutants escaping the combustion chamber and entering the effluent stream of the incinerator have caused significant air pollution problems. This type of problem has resulted in the abandonment of at least one large-scale incineration facility for pesticide wastes. Evidently, little is known about the characteristics of the particulates and gases in the exhaust streams of incinerators burning the liquid wastes associated with pesticide manufacturing.

i. Almost every pesticide manufacturing plant contacted during this study utilized some form of burial as a method of disposal of at least a portion of their processed waste. In most cases little study of the migration rate of the toxic components of the waste to be buried had been undertaken. Since many of the plants utilized contract disposal services, they felt little responsibility for studying the effect of the compound on the surrounding underground environment. Therefore, very few problems associated with burial practices were reported. Perhaps the most often mentioned problem concerning burial as a disposal method was sloppy handling techniques at the burial site. In some cases, poor handling resulted in blowing dust, spilled liquids, and surface runoff contamination during rainy periods.

j. Ocean disposal and deep well injection are two methods that are being used in the pesticide manufacturing industry. These methods are discussed in the report but are not recommended as practices to be considered in the future. Uncertainties associated with these disposal methods have caused considerable pressure to be placed on regulatory agencies. As a result these methods will probably be severely restricted in the future.

15. The cost associated with the treatment of pesticide manufacturing wastes is difficult to determine on a generalized basis. It can be assumed that the cost associated with treating pesticide manufacturing wastewaters biologically will be somewhat higher than the treatment of most petrochemical wastewaters of similar organic loading. Longer detention times are generally required to insure accurate degradation of the toxic components. Chemical and physical treatment methods must be highly effective and are usually expensive. These systems should be designed for the particular waste involved and the cost will vary widely depending on the toxicity of the waste and its resistance to chemical and physical treatment. The costs of incineration are a function of the volume of the waste that is to be burned, the corrosive nature of the waste and its fuel value as well as the air pollution control equipment required to prevent atmospheric contamination. Little detailed cost information could be obtained for the incineration units presently in use. Burial and ocean disposal costs can be estimated quite easily and some figures are included in this report. It appears that in the short term these two methods can be very inexpensive if conducted on a relatively large scale. However, increased regulatory constraints will no doubt have some effect on these costs.

16. Without more information on waste stream quality, toxicity and flows, it is impossible to isolate areas of the pesticide industry where the problems may be more pressing. From the information compiled during this study, it is evident that progress is being made in the area of pesticide manufacturing waste treatment, but severe problems still remain. The most enlightening facet of this study was that in several cases, the people involved did not or would not realize that a problem did exist. Therefore, to say that one type of pesticide or manufacturing process poses a more severe problem than another would be misleading. With proper process design, plant control and waste treatment, most, if not all, pesticide manufacturing wastes can be discharged safely. Plant operators must be made aware of the need for proper waste management and the control measures which can be beneficial. Many manufacturers in all phases of pesticide production have realized this and have been successful in reducing environmental contamination from pesticide manufacturing wastes. Others have not.

CHAPTER II

RECOMMENDATIONS

1. Pesticide manufacturing wastes are composed of a wide variety of compounds, some of which are active as pesticidal agents and many of which are not. In order to gain a more complete understanding of the problem, all pesticide manufacturers should be required to periodically submit detailed analyses of all waste streams discharged from their plants. Convenient forms should be designed to permit computer logging, retrieval, and analysis of the submitted data. The analytical requirements should be specified to insure that the manufacturer is aware of the composition of his waste discharges and the potential each component has for producing environmental stress. These analyses should not be limited to liquid wastes but should also include incinerator off-gases and the semi-solids and solids which are buried.

2. Often plant operators indicated that the composition of individual waste streams from single units or small areas of the plant was unknown. It is recommended that all plant managers be encouraged to examine the individual waste streams before they are combined. In some cases a portion of the wastewater produced in the plant may be easily treated or recycled before it is contaminated with acids, solvents, active pesticidal compounds, etc. In addition, careful study may show that one waste stream may be useful in treating another. As an example, it was found that a substantial reduction in chemical requirements for neutralization occurred if a caustic rinse stream was mixed with an acid waste after the acid stream passed through a limestone trench rather than before trench treatment.

3. Conversely, water reuse and waste stream separation should be studied carefully before steps are taken to institute such practices. The effects of concentrating the waste stream on its treatability and potential for causing environmental stress should be considered.

4. Pesticide manufacture and pesticide manufacturing waste treatment are sensitive areas. Due to the increasing public and governmental attention directed toward pesticides, many manufacturers are hesitant to discuss these matters outside the company. Therefore, it is recommended that a detailed study of waste treatment practices be initiated through an industry-sponsored organization that would have ready access to design

data, operational parameters, cost information, treatability data and treatment efficiency information. The detailed design and operational data could be published in the form of a manufal similar to but more detailed than the manual Waste Disposal, published by the Agricultrual Chemical Association in 1966.

5. Since most chemical and biological waste treatment systems are sensitive to rapid changes in wastewater quality, continuous monitoring equipment should be installed at strategic points through a plant to detect unusual conditions indicative of spills or upsets which might produce toxic "slugs" in the wastestream. Diversion and storage facilities should be provided to protect the treatment systems. Research is needed to facilitate the development and production of reliable detectors capable of providing the desired response to changes in waste stream quality. This type of protection may be partially attainable with a large holding pond before the treatment system, but in the use of some highly toxic compounds, even large ponds may prove to be inadequate.

6. Most pesticide removal work has been conducted using low levels of active compounds in drinking water. Similar studies should be conducted to determine the effectiveness of removal processes such as chemical coagulation, clay adsorption, carbon adsorption, foam fractionation, ozonation, etc. on waste streams containing relatively high concentrations of active pesticides, high concentrations of organics and high concentrations of dissolved solids.

7. Many pesticide manufacturing aqueous waste streams contain high concentrations of dissolved solids. These solids may cause significant problems in chemical and biological treatment systems, incinerators, deep wells and evaporation ponds. In-depth studies of the problems associated with the high salt concentrations (10,000 - 100,000 mg/l) typical of pesticide manufacturing wastes should be conducted to determine the feasibility of "conventional" industrial waste treatment systems.

8. Kinetic data on physical and chemical treatment processes for pesticidal wastes are limited. Investigations of reaction rates and dose-time-effectiveness relationships for commonly used chemical agents in typical pesticide manufacturing wastewater streams should be conducted. The kinetics of the reactions and the end products of the reactions should be determined.

9. Neutralization is required for most pesticide manufacturing liquid wastes. These highly buffered acidic or basic streams often require massive chemical doses to produce desirable pH levels. At these dose levels a thorough understanding of reaction rates, product formation and possible interference with further reaction, mixing requirements, and mass transfer are of importance. Engineering designs could include the consideration of these factors if research into the application of the basic neutralization theory was conducted to obtain usable design data.

10. The effect of neutralization chemicals on subsequent chemical, physical or biological treatment schemes may also be significant. Investigations of the effects of various neutralization agents on the wastewater quality and treatability should be conducted. In addition, the large sludge volumes resulting from these massive chemical doses can produce significant solid waste problems which should be considered. The toxicity, stability, and leach rates of these sludges should be investigated.

11. Biological waste treatment appears to be a reasonable scheme for handling many types of pesticidal wastes. However, design criteria and operational data for waste streams containing active pesticidal agents are sketchy. Full-scale or pilot studies should be conducted to better determine parameters such as loading rates, detention times, allowable "toxic" concentrations, MLVSS, oxygen requirements, etc., which are necessary to achieve optimum efficiency with representative waste streams. In addition, the presence or absence of potentially harmful degradation products should be investigated for "high rate" biological systems treating complex pesticidal waste streams.

12. The rate of removal of soluble organics by a biological wastewater treatment system appears to be significantly affected by the wastewater temperature. Detailed investigations of the temperature dependence of pesticidal compound degradation (as well as other soluble organic materials) should be conducted to insure that systems are designed with adequate capacity to handle the pesticidal and organic loads during the winter months when biological activity is reduced. This temperature effect is not limited to pesticide manufacturing wastes but affects biological systems for any industrial wastewater containing a high percentage of soluble organic material.

13. Incineration appears to be an effective waste disposal method for pesticide manufacturing wastes, but several problem areas should be investigated. These include:

a. The gaseous and particulate emissions resulting from incineration of wastes which have been treated with various neutralization agents should be characterized. Detailed analysis of the flue gases produced under field conditions should be conducted for "typical" wastes burned in several types of multichamber, vortex, and fluidized bed units.

b. Methods of minimizing undesirable gases and particulates through combustion control, air flow control, incineration design, waste stream modification and exhaust cleaning should be studied for pesticidal waste streams.

c. Visible plumes often result from the high temperature burning of pesticide wastes. These persistent fogs might be reduced or eliminated by proper burning and particulate removal. Studies should be conducted to determine ways by which these visibility problems can be reduced when wastes containing high levels of dissolved solids are burned. The particle size, size distributions, mass emission rates, nucleating potential, etc. should be determined.

d. In general ash disposal from incineration was not considered a problem, but research should be conducted in this area to determine the possible effect of this ash on the environment, and the potential for recovery of usable products from this waste material.

14. Some pesticide manufacturing wastes are discharged into conventional municipal waste treatment facilities. Often a portion of the active compounds passes through the system. Studies should be conducted to determine the effect of conventional treatment systems on the diluted wastes and the effect of the pesticide compound on the conventional system.

15. Many pesticide manufacturing operations are a part of a large petrochemical complex and the pesticidal wastes are mixed with the other petrochemical waste streams for treatment in a common system. The effectiveness of these industrial waste treatment systems on the active pesticidal compounds should be determined.

16. Many long-lived pesticides tend to concentrate in certain areas of the environment. For example, DDT in a wastewater discharge will result in a build up of DDT and its degradation products in the sediments near the discharge point. The sediment concentrations may be several orders of magnitude higher than the concentration of pesticides in the water. Therefore, it is recommended that studies of the distribution of various long-lived compounds in environmental systems be investigated to determine those compounds which may pose significant threats, even at low initial concentrations.

17. If rapid progress is to be made in reducing the amount of pesticidal wastes discharged, information on present practices and problems must be made available to researchers, plant operators, and control agencies. More discussion and more rapid exchange of information will be required if the complex problems associated with airborne and waterborne pesticidal agents are to be understood and solved.

CHAPTER III

PESTICIDE PRODUCTION AND USE

Definition of Pesticides

Pesticides are chemical compounds used to destroy organisms that are considered by man to be "pests". They are usually classified (according to the target organism) as insecticides, herbicides, fungicides, rodenticides, miticides, acaricides, and nematocides. Figure 1 shows the relative importance of the types of pesticides; heavy arrows for herbicides and insecticides indicate that they are more widely used than the other pesticides.

Pesticides include both organic and inorganic materials. Examples of inorganic pesticides include compounds of lead, arsenic, mercury, chlorine, Paris Green (Arsenical), lime-sulfur washes, hydrogen cyanide, lead arsenate, sodium arsenite, metal salts (copper, zinc, chromium, and thallium), and toxic compounds of fluorine and sulfur. Examples of naturally occurring organic pesticides are rotenone, pyrethrin, red squill, sabadilla, nicotine, and petroleum derivatives. Examples of synthetic organic pesticides are DDT (dichloro diphenyl trichloroethane), BHC (benzene hexachloride), chlordane, methoxychlor, aldrin, dieldrin, parathion, malathion, toxaphene, 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), captan, zineb, and barbaryl (Sevin). A more complete list of widely used pesticides is contained in Appendix A.

Trends in Production and Use

The extent to which the pesticide industry has changed over the years can be readily grasped by considering that more than 80% of this industry's output now comes from organic chemicals, while in the 1940's the industry depended almost entirely on inorganic materials. The shift is illustrated by the decrease in output of lead arsenate and calcium arsenate which were the backbone of the pre-war pesticide industry.

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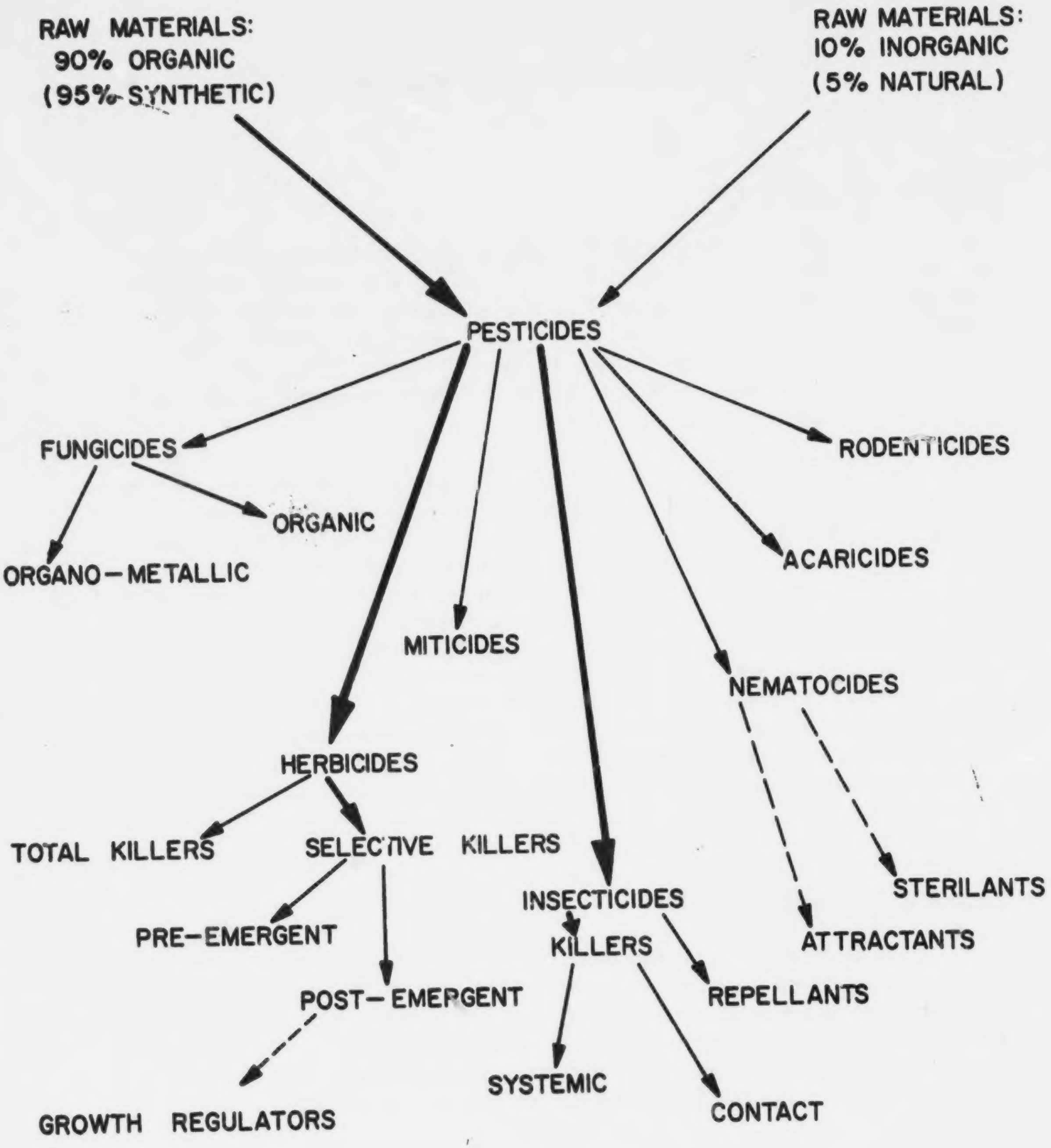
RAW MATERIALS:
90% ORGANIC
(95% SYNTHETIC)
RAW MATERIALS:
10% INORGANIC
(5% NATURAL)
PESTICIDES
FUNGICIDES
RODENTICIDES
ORGANIC
ORGANO-METALLIC
ACARICIDES
MITICIDES
NEMATOCIDES
HERBICIDES
TOTAL KILLERS
SELECTIVE KILLERS
STERILANTS
INSECTICIDES
PRE-EMERGENT
KILLERS
ATTRACTANTS
POST-EMERGENT
REPELLANTS
SYSTEMIC
GROWTH REGULATORS
CONTACT

Figure 1. Classification and Relative Importance of Pesticides (Anon., Chem. Engr., 1969)

Table 1. Decrease in Inorganic Pesticide Usage in the U.S.

Year	1940	1960	1965	1967	1968
Lead arsenate (million pounds)	75	10	7	6	9
Calcium arsenate (million pounds)	50	7	4	2	3

Source: Anon., Chem. Engr., 1969.

Highly chlorinated organic compounds have followed the same trend (Table 2). BHC (benzene hexachloride), for instance, has been gradually displaced by the dieldrin-heptachlor class of compounds which are more specific and effective. In contrast, the production of DDT has fluctuated erratically and is now below its peak of the early 1960's, but may continue to be used in significant quantities (Anon., Chem. Engr., 1969).

With the appearance of resistance to DDT by a number of organisms, a large group of new pesticides has appeared (first the organophosphates, then the carbamates, and others). There are now in the U.S. some 900 active pesticidal chemicals formulated into over 60,000 preparations (Mrak, et al., 1969). Recent regulations limiting or banning the use of DDT under certain conditions may have a marked effect on its future production, as well as the production of "replacement compounds." However, the high costs involved in developing and testing new pesticides for marketing have risen to 3-6 million dollars per product and will tend to reduce the number of new chemicals reaching the market.

Recent Production and Sales Data

Production of the major pesticides for 1960-1969 is given in Table 3. Trends in pesticide usage are obvious. As indicated more clearly in Table 4, changes are occurring in the popularity of certain pesticides. Since 1966 the percentage of pesticides classified as fungicides (on a weight basis) has dropped from 14.4 % to 13.3% in 1969 and the insecticide percentage has decreased from 58.7% of the market to 53.2%. Herbicide use during the same period increased from 26.9% of the market to 33.5%. The chlorinated hydrocarbon type herbicide usage has decreased, but the substitute compounds have more than made up for the decrease.

Table 2. Production Decline of Chlorinated Pesticides in U.S.

Year	Annual Production, Million Lbs.			
	BHC	DDT	Others*	Total
1952	85	100	---	185
1954	77	97	45	219
1956	85	138	87	310
1958	31	145	98	274
1960	37	164	91	292
1962	12	167	106	285
1964	< 6	124	105	240**
1966	< 6	141	119	260**
1967	--	103	120	223**
1968	--	139	116	255**
1969	--	123	110	233**

*Dieldrin, aldrin, toxaphene, heptachlor, chlordane, endrin, terpene polychlorinates.

**Estimate.

Source: U.S. Tariff Commission Statistics, Chem. Engr., 1969.

Table 3. U.S. Pesticide Production (Annual Production - Thousand Lb.)

Compound	1960	1962	1964	1965	1966	1967	1968	1969
Calcium arsenate	6,590	4,660	6,958	4,192	2,890	2,040	3,398	---
Lead arsenate	10,062	9,990	9,258	7,098	7,328	5,952	9,016	---
Copper sulfate	116,000	79,968	83,768	94,656	103,416	80,256	87,568	101,136
Aldrin toxaphene group [a]	99,671	106,276	105,296	118,832	130,470	120,183	115,974	---
Benzene hexachloride[b]	37,444	12,022	---	---	---	---	---	---
DDT	164,180	167,032	123,709	140,783	141,349	103,411	139,401	---
Methyl bromide	12,659	12,757	16,994	14,303	16,345	19,665	20,454	---
Parathion	7,434	8,786	12,768	16,607	19,444	11,361	---	---
Ferbam	2,529	2,966	1,838	2,384	1,379	2,331	1,900	---
Nabam	2,978	4,216	2,251	2,489	2,053	1,361	---	---
Zineb	---	---	6,664	5,075	4,721	3,055	3,081	---

Table 3. (Continued)

Compound	1960	1962	1964	1965	1966	1967	1968	1969
2,4-D acid	36,185	42,997	53,714	63,320	68,182	77,139	79,263	47,077[c]
2,4,5-T acid	6,337	8,369	11,434	11,601	15,489	14,552	17,530	---
Methyl parathion	11,794	16,156	18,640	29,111	35,862	33,344	38,163	17,938[c]
Other organic pesticides	227,229	348,967	437,943	477,148	577,816	663,261	694,421	---

[a] Includes the chlorinated compounds aldrin, chlordane, dieldrin, heptachlor, and toxaphene.

[b] Gross production (gamma isomer content was 7.7 million pounds in 1961, 3.4 million pounds in 1962, and 1.8 million pounds in 1963); no data since 1963.

[c] Preliminary

Source: U.S. Tariff Commission Statistics, 1969.

Table 4. Synthetic Organic Pesticides: Volume and value of sales by classes, U.S., 1966-1969

VOLUME OF SALES

Class	1966		1967		1968		1969	
	Amount	% of Total	Amount	% of Total	Amount	% of Total	Amount	% of Total
	1000 lbs		1000 lbs		1000 lbs		1000 lbs	
Fungicides	118,397	14.4	120,413	13.4	129,961	13.5	124,418	13.3
Herbicides & plant hormones	221,502	26.9	287,582	32.1	318,554	33.2	311,158	33.5
Insecticides, fumigants, rodenticides and soil conditioners	482,357	58.7	489,368	54.5	511,116	53.3	493,088	53.2
Total	822,256	100	897,363	100	959,631	100	928,663	100

Table 4. (Continued)

VALUE OF SALES

Class	1966 Amount	1966 % of Total	1967 Amount	1967 % of Total	1968 Amount	1968 % of Total	1969 Amount	1969 % of Total
	$1000		$1000		$1000		$1000	
Fungicides	53,275	9.1	56,333	7.2	62,061	7.3	61,174	7.2
Herbicides & plant hormones	257,635	44.1	429,980	54.6	483,330	56.9	495,670	58.2
Insecticides, fumigants, rodenticides and soil conditioners	272,892	47.3	300,730	38.2	303,849	35.8	294,322	34.6
Total	583,802	100	787,043	100	849,240	100	851,166	100

Source: U.S. Tariff Commission Statistics, 1969.

Table 5. Pesticides and Related Products: U.S. Production and Sales, 1969

[Listed below are all pesticides and related products for which any reported data on production or sales may be published. (Leaders are used where the reported data are accepted in confidence and may not be published or where no data were reported.)]

Product	Production	Sales		
		Quantity	Value	Unit Value
	1,000 pounds	1,000 pounds	1,000 dollars	per pound
Grand Total	1,104,381	928,663	851,166	$0.92
PESTICIDES AND RELATED PRODUCTS, CYCLIC				
Total	819,748	666,038	697,167	1.05
Fungicides, total	100,748	84,384	34,557	.41
3,5-Dimethyl-1,3,5-2H-tetrahydrothiadiazine-2-thione (DMTT)	1,074	1,102	517	.47
Mercury fungicides, total	1,475	1,298	6,792	5.23
Phenylmercuric acetate (PMA)	534	351	2,467	7.03
Phenylmercuric oleate	407	381	1,126	2.96
Other mercury fungicides	534	566	3,199	5.65
Naphthenic acid, copper salt	1,545	1,529	438	.29
Pentachlorophenol (PCP)	45,988	40,566	5,946	.15
8-Quinolinol (8-Hydrozyquinoline), copper salt	88	205	285	1.39
All other fungicides	50,578	39,684	20,579	.52

Table 5. (Continued)

Product	Production	Sales		
		Quantity	Value	Unit Value
	1000 pounds	1000 pounds	1000 dollars	per pound
Herbicides and plant hormones, total	324,221	250,069	445,275	1.78
1,2-Dihydropyridazine-3,6-dione (Maleic hydrazide) (MH)	2,771	---	---	---
Phenozyacetic acid derivatives:				
2,4-Dichlorophenizyacetic acid (2,4-D)	47,077	18,786	5,224	.28
2,4-Dichlorophenozyacetic acid esters and salts, total	56,998	46,057	14,627	.32
2,4-Dichlorophenozyacetic acid,n-butyl ester	3,403	2,675	1,200	.45
2,4-Dichlorophenozyacetic acid,sec-butyl ester	4,992	---	---	---
2,4-Dichlorophenozyacetic acid, dimethylamine salt	22,403	20,270	6,347	.31
2,4-Dichlorophenozyacetic acid,iso-octyl ester	11,093	8,384	2,449	.29
All other (2,4-D) esters and salts	15,107	14,728	4,631	.31
2,4,5-Trichlorophenozyacetic acid (2,4,5-T)	4,999	---	---	---
2,4,5-Trichlorophenozyacetic acid esters and salts, total	11,626	5,697	5,963	1.05
2,4,5-Trichlorophenozyacetic acid, n-butyl ester	258	524	452	.86
2,4,5-Trichlorophenozyacetic acid, iso-octyl ester	4,187	2,974	3,393	1.14
All other (2,4,5-T) esters and salts	7,181	2,181	2,118	.97
2-(2,4,5-Trichlorophenozy) propionic acid (Silvex)	1,597	---	---	---
All other cyclic herbicides and plant hormones	199,153	179,547	419,461	2.34

Table 5. (Continued)

Product	Production	Sales		
		Quantity	Value	Unit Value
	1000 pounds	1000 pounds	1000 dollars	per pound
Insecticides and rodenticides, total	394,467	331,585	217,335	.66
Aldrin-toxaphene group	---	110,366	50,228	.46
α-Bis (p-chlorophenyl) - β, β, β -trichloroethane (DDT)	123,103	80,305	11,032	.14
Organophosphorus insecticides, total	92,458	70,361	73,190	1.04
0, 0-Dimethyl 0-p-nitrophenyl phosphorothioate (Methyl parathion)	50,572	32,818	15,794	.48
All other organophosphorus insecticides	41,886	37,543	57,396	1.53
All other insecticides and rodenticides	178,906	70,553	82,885	1.17
PESTICIDES AND RELATED PRODUCTS, ACYCLIC				
Total	284,945	262,625	153,999	.59
Fungicides, total	39,805	40,034	26,617	.66
Dimethyldithiocarbamic acid, ferric salt(Ferbam)	---	1,771	645	.36
Ethylene bis (dithiocarbamic acid), disodium salt (Nabam)	1,938	1,989	880	.44
All other acyclic fungicides	37,867	36,274	25,092	.69
Herbicides and plant hormones	69,085	61,088	50,395	.82

Source: U.S. Tariff Commission Report, 1969.

Forecasts in Production and Use

The production and use of pesticides in the U.S. is expected to continue to grow at an annual rate of approximately 16%. Predictions are that insecticides will more than double in use in five years and herbicides will increase at a more accelerated pace (perhaps 20% annually). The foreign use of pesticides will likewise continue to increase with the organochlorine and organophosphorus insecticides continuing to represent a significant part of the foreign market (Mrak, *et al.*, 1969).

Sales predictions based on a survey of 13 of the industry's leading producers (companies which account for well over half of the pesticide sales in the U.S.) show a $187 million increase in U.S. sales of technical synthetic organic pesticides in 1970 and a $651 million jump by 1975. These manufacturers project the $1.5 billion pesticide market in 1975 will be as follows: fungicides, $75 million; insecticides, $526 million; herbicides, $950 million (Anon., *Industry and Business*, 1970). Figure 2 graphically shows past and predicted pesticide production (including exports) in the U.S. Presently 32 of the major pesticides account for more than 50% of the total sales of unformulated pesticides. The projected growth of these market leaders is given in Table 6.

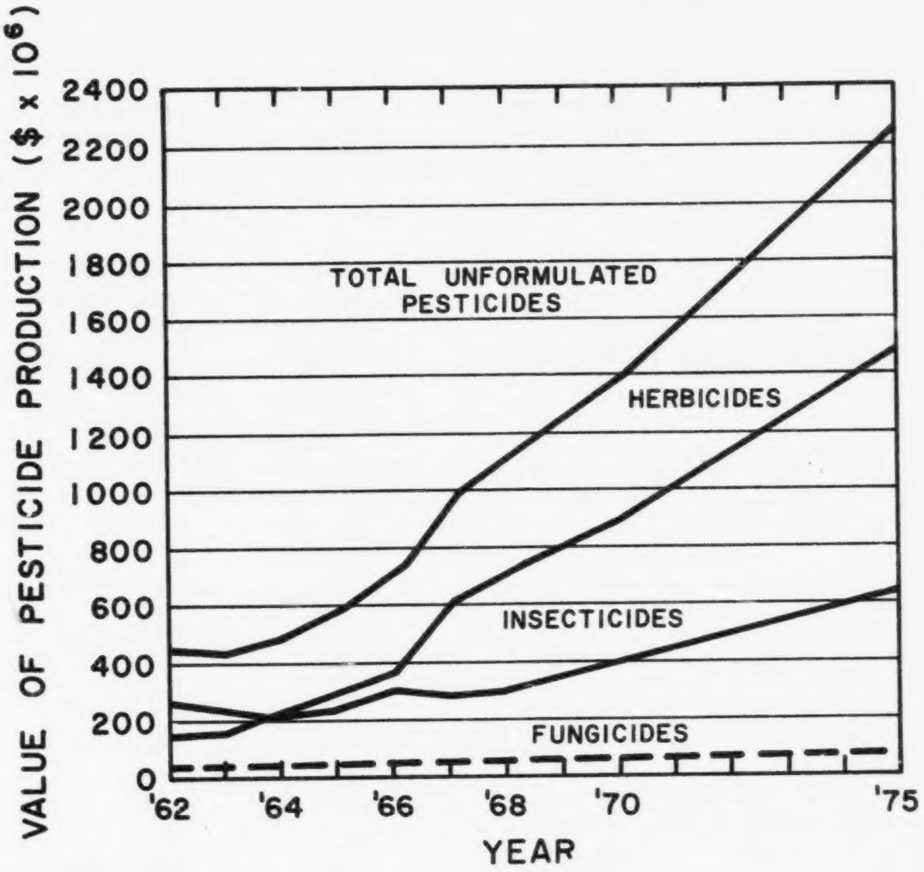

Figure 2. Past and Projected Pesticide Production in the U.S.

Source: Neumeyer, _et al._, 1969.

Table 6. Principal Products

Dominant Pesticide Products

Products, annual sales	Projected Sales Growth	Type	Chemical Classification
$25 million & over			
Atrazine	5-10%	Herb.	Chl. Hyd.
Treflan	15-20%	Herb.	Syn. Org.
Sevin	5-10%	Inst.	Carb.
Amiben and Related Products	15-20%	Herb.	Chl. Hyd.
Malathion	10-15%	Inst.	O.P.
2, 4-D	5-10%	Herb.	Chl. Hyd.
$10-25 million			
Aldrin	0-5%	Inst.	Chl. Hyd.
Ramrod, Randox & Related Products	10-15%	Herb.	Chl. Hyd.
Diazinon	5-10%	Inst.	O.P.
Toxaphene	0-5%	Inst.	Chl. Hyd.
DDT	decline	Inst.	Chl. Hyd.
Methyl Parathion	0-5%	Inst.	O.P.
Parathion	decline	Inst.	O.P.
Guthion	10-15%	Inst.	O.P.
Planavin	20%+	Herb.	Syn. Org.
Endrin	0-5%	Inst.	Chl. Hyd.
Dithiocarbamates	0-5%	Inst.	Carb.
Captan	5-10%	Inst.	Chl. Hyd.
Chlordane	10-15%	Inst.	Chl. Hyd.
Heptachlor	decline	Inst.	Chl. Hyd.
$5-10 million			
2, 4, 5-T	10-15%	Herb.	Chl. Hyd.
Tordon	15-20%	Herb.	Chl. Hyd.
Methyl Bromide	decline	Fum.	Syn. Org.
Knoxweed (EPTC, 2, 4-D)	10-15%	Herb.	Carb.
Disyston	10-15%	Inst.	O.P.
Thimet	10-15%	Inst.	O.P.

Table 6. (Continued)

Products, annual sales	Projected Sales Growth	Type	Chemical Classification
Pentachlorophenol	0-5%	Fung.	Chl. Hyd.
Methyoxychlor	5-10%	Inst.	Chl. Hyd.
Kelthane	0-5%	Inst.	Chl. Hyd.
Bux-Ten	15-20%	Inst.	Carb.
Cyprex	10-15%	Fung.	Syn. Org.
Paraquat	0-4%	Herb.	Syn. Org.
Banvel	15-20%	Herb.	Chl. Hyd.

Source: Neumeyer, et al., 1969.

Legend:

Carb. = carbamate
Chl. Hyd. = chlorinated hydrocarbon
Syn. Org. = synthetic organic
O. P. = organophosphorus

CHAPTER IV

PESTICIDE MANUFACTURE

This chapter will include brief discussions of the manufacturing processes utilized to produce several of the major types of pesticides. Since many of these processes are presently covered by patents, information of kinetics, yields, waste products and product purity is limited. General process descriptions taken from various literature sources will be given and waste stream characteristics as reported by manufacturers will be included without modification.

Producers of Pesticides

Dow Chemical and E. I. duPont de Nemours, followed by Union Carbide, are the largest producers of pesticides in the U.S. Next in sales volume are American Cyanamid, Rohm and Haas, Stauffer Chemical, Velsicol Chemical, and Chemagro--all of which have specialized in a particular area. For instance, Chemagro produces a complete line of phosphate insecticides and miticides developed by Bayer in West Germany. FMC Corp., which acquired Niagara Chemical, is typical of many other companies that entered the pesticide business by acquisition. Oil companies such as Standard Oil of California (Ortho brand products) and Shell (Vapona brand), and drug companies such as Geigy and Elanco also produce significant quantities of pesticides (Anon., *Chem. Engr.*, 1969).

Manufacturing Processes and Waste Generation

The patent literature contains valuable information on the numerous processes for the manufacture of pesticides. A collection of processes for 84 important pesticides is found in *Pesticide Production Processes* (Sittig, 1967). However, in many cases a certain amount of "art" that cannot be described in the literature is required to produce a pure product or achieve 90% reaction rather than 60%. Therefore, product quality and waste stream characteristics will vary significantly, even for the same product and process.

The basic manufacturing processes for some of the more widely-used pesticides are described in the following discussion.

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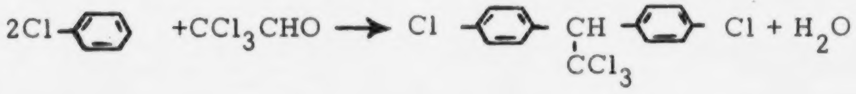
DDT

DDT (Dichloro-diphenyl-trichloroethane) is a name that covers 27 possible isomers, the most active of which is 1,1,1-trichloro-2, 2-bis (chlorophenyl) ethane. DDT was one of the first pesticides manufactured on a large scale and easily holds the record for the greatest volume of any organic pesticide ever produced. Its manufacture is relatively simple; it is made by condensing monochlorobenzene and chloral in the presence of concentrated sulfuric acid (Sittig, 1967).

The reaction can be represented by the following equation:



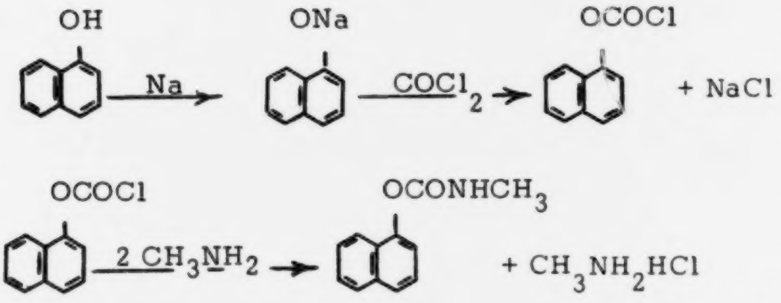
The biggest problems in DDT manufacture are in the recovery of unconverted ingredients and in steering the reaction toward production of the desired isomer. The reaction is kept below 30°C and takes place at atmospheric pressure in a stirred batch reactor system.

DDT recovery (according to U.S. Patent 2,932,672, Diamond Alkali) is by crystallization. Impure DDT crystals are washed with a caustic solution, and unreacted monochlorobenzene is removed by melting the crystals and bubbling steam through the melt. The purified crystals are then dried and flaked (Anon., Chem. Engr., 1969).

The wastes resulting from the process include spent acids (hydrochloric and sulfuric), monochloral benzene, sodium monochloral benzene sulfonate, chloral, NaOH caustic washwaters, chlorobenzene, sulphonic acid, and some product. The waste streams may contain DDT in the 1-5 ppm range with DDE and other related compounds present in amounts up to four times the DDT level. The pH of the waste is low and the salt content is high. Information on DDT waste stream characteristics including BOD, COD, toxicity, TDS, flow, etc. were not made available by any of the manufacturers contacted during this study.

Carbaryl (Sevin)

The largest volume carbamate insecticide is 1-naphthyl, N-methyl carbamate. According to Union Carbide, carbaryl (Sevin) is manufactured from alpha-naphthol, phosgene, and methylamine--all of which are readily available. There are three reaction steps. Alpha-naphthol reacts with sodium 1-naphthoxide, which in turn, is reacted with phosgene; the resulting chloroformate is reacted with methylamine as follows:



The carbamate which crystallizes is easily separated (U.S. Patent 2,903,478). Excess amine must be added to remove the hydrochloric acid formed in the reaction. Considerable care, through the use of special scrubbers and by enforcing safety precautions, must be taken to ensure that phosgene does not escape to the atmosphere. Wastewaters contain high total solids, but almost no suspended solids and little pesticidal compounds. A typical waste stream from carbamate manufacture will contain:

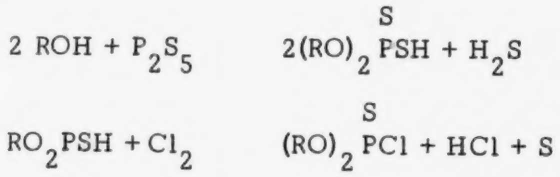
COD	10,000 mg/l
BOD_5	Nil
Total Solids	40,000
pH	7-10
Suspended Solids	Nil
Sodium	8,000
Chlorides	100
Phosphates	Nil
Organic Nitrogen	500

Sulfates	20,000
Product	Nil
Toxicity	Low
Flow per pound of product	Not available

Parathion and Methyl Parathion

These materials are both manufactured from sodium p-nitrophenolate; methyl parathion is formed by reaction 0,0-dimethyl phosphorothiochloridate with the sodium compound, and parathion, from the reaction of the equivalent 0,0-diethyl compound.

There are three steps involved in the synthesis of both parathion and methyl parathion: one common method involves the reaction of the appropriate alcohol (methyl or ethyl alcohol) with phosphorus pentasulfide, followed by chlorination.



$$2\ ROH + P_2S_5 \qquad 2(RO)_2\overset{S}{P}SH + H_2S$$

$$RO_2PSH + Cl_2 \qquad (RO)_2\overset{S}{P}Cl + HCl + S$$

The phosphorothoro-chloridate is then reacted with sodium p-nitrophenoxide, forming the final product

$$(RO)_2PCl + NaOC_6H_4NO_2 \quad (RO)_2POC_6H_4NO_2 + NaCl$$

(Anon., Chem. Engr., 1969)

The waste streams from parathion manufacture may contain sulfur, HCl, sodium chloride, sodium carbamate, trimethyl theophosphate, and other organics including paranitrophenol and small amounts of product. A typical waste stream can be characterized by:

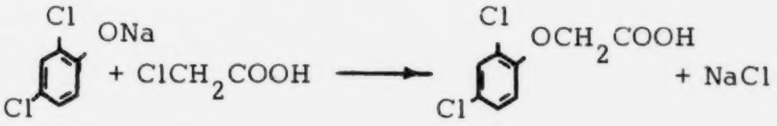
COD	3,000 mg/l
BOD	700
Total Solids	27,000
pH	2.0

Acidity	3,000
Sodium	6,000
Chlorides	7,000
Phosphates	250
Nitrates	20
Sulfates	3,000
Parathion	20
Calcium	High

Gaseous emissions from parathion production contain significant amounts of mercaptans including hydrogen sulfide. Concentrated residues and tank bottoms must also be handled since they contain large amounts of intermediates and some product. This portion of the waste may be a slurry with a paste-like consistency which poses severe handling problems (Stutz, 1966), but seldom enters the wastewater stream.

2,4,5-T, 2,4-D and MCPA Herbicides

The major aromatic-based.herbicides are 2,4,5-T (2,4,5-trichlorphenoxyacetic acid); 2,4-D (2,4-dichlorphenoxyacetic acid), and MCPA (2-methyl, 4-chlorophenoxy acetic acid). Their synthesis begins with the reaction of monochloracetic acid with a phenol group. The phenoxy group, which is produced in this reaction, appears in these three herbicides in a 2,4-DEP ("Falone"), and many other herbicides. The general reaction of monochloracetic acid with phenol is via sodium phenate. The process used for 2,4-D, the most widely sold product of the chlorinated herbicide manufacturing process, is typical. Monochloracetic acid is condensed with the dichlorphenate in an alkaline solution at atmospheric pressure and 60 to 80°C for six to eight hours in a jacketed stirred reactor; no catalyst is necessary. The reaction may be described by:



When the reaction is complete, excess 2,4-dichlorophenoxide is decomposed by acidifying the mixture to pH 5. The 2,4-dichlorophenol is removed by steam distillation and recycled. By reducing the pH to about 1, the 2,4-D acid precipitates from the reaction mixture and can then be filtered, washed and dried. Esters of the 2,4-D acid are used as herbicides. The other chlorinated herbicides are produced in a similar manner.

For 2,4,5-T manufacture, a solvent is added to the reaction system to produce the required reaction temperature of 100-180°C, and the rate of reaction is faster than that for 2,4-D production. MCPA is made by chlorinating methyl phenoxyacetic acid which comes from the reaction of monochloracetic acid with the sodium salt of ortho-cresol.

The waste stream from chlorinated hydrocarbon herbicides includes large amounts of sodium chloride, hydrochloric acid, some caustic, and organics including solvents, phenols, chlorophenols and chlorophenoxy acids. These wastes arise from acidification, washing steps, phase separation steps, incomplete yields and chlorination of the phenolic compounds. A typical waste stream can be characterized by:

COD	8,300 mg/l
BOD_5	6,300
Total Solids	104,000
Suspended Solids	2,500
pH	0.5
Chlorides	52,000
Chlorophenols	112
Chlorophenoxy Acids	235
Nitrogen	Low
Phosphorus	Low
Flow	30 # COD/ # Product

The chlorinated herbicide wastes can vary considerably from plant to plant and even in the same plant as indicated by the data in Table 7.

Diolefin-based Insecticides (Aldrin, Dieldrin, Endrin, Chlordane and Heptachlor)

This group of insecticides is derived from cyclopentadiene, and from hexachlorocyclopentadiene. Hexachlorocyclopentadiene can be

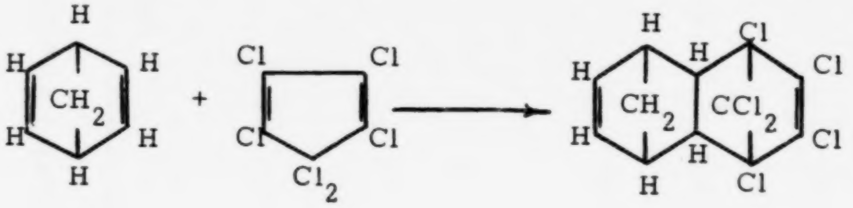
Table 7. Waste Characteristics of Chlorinated Herbicide Wastes

Analysis	2, 4, 5-T Acid Waste			2, 4-D Acid Waste		
	Sample #1	Sample #2	Sample #3	Sample #1	Sample #2	Sample #3
pH	7.5	7.9		8.5	9.5	
COD (mg/l)	21,700	25,700	19,600	27,500	23,600	22,700
BOD $_5$ (mg/k)*	16,800	*	13,400	16,700	*	13,000
Chlorides (mg/l)	96,300	69,000		144,000	72,000	
Total Solids (mg/l)		172,467			167,221	
Total Volatile Solids (mg/l)		18,150			22,100	
Suspended Solids (mg/l)		700			348	
Volatile Suspended Solids (mg/l)		242			83	
Total Kjeldahl Nitrogen (mg/l)		40			45	
Odors		Not Offensive			Not Offensive	

*16,680 mg/l using 50-50 dilution of 2,4-D and 2,4,5-T and acclimated seed (below toxic levels)

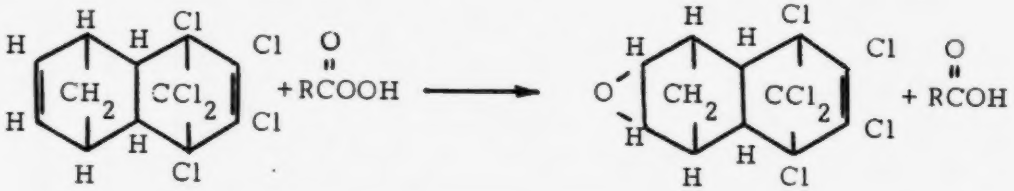
Source: Ford & Gloyna "Confidential Report" 1967.

produced from a reaction of n-pentane and chlorine as described by J. T. Patton, et al. in U.S. Patent 2,960,543. Cyclopentadiene may be produced by vapor phase cracking of naphtha. Aldrin (1,2,3,4,10-hexachloro-1,4,4a,5,8-hexahydro-1,4-endo-exo-5, 8 dimethanonaphthalene) may be produced under slight pressure and elevated temperatures by the reaction of hexachlorocyclopentadiene with bicycloheptadiene, according to the equation:

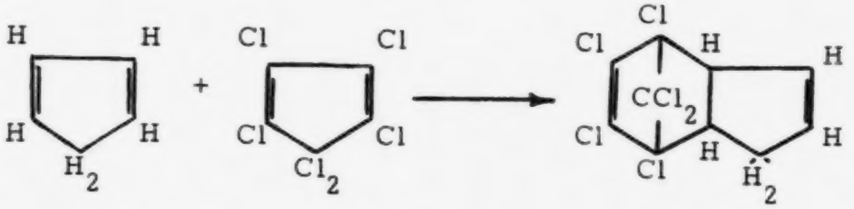

H
H
H
CH2
H
H
H
+
Cl
Cl
Cl
Cl
Cl2
H
Cl
H
Cl
H
CH2
CCl2
H
H
Cl
H
Cl

Toluene may be used as a solvent in the reaction.

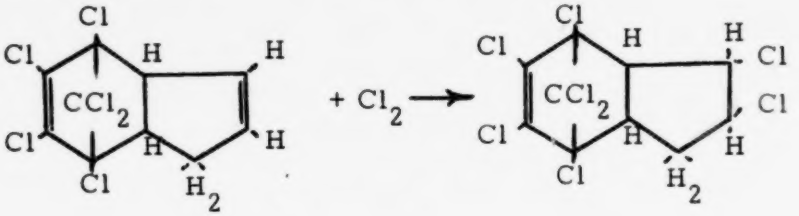
Dieldrin may be produced by epoxidizing aldrin with a per-acid:


H
H
Cl
H
Cl
O
CH2
CCl2
+RCOOH
H
Cl
H
H
Cl
H
Cl
H
H
Cl
O
O
CH2
CCl2
+ RCOH
H
Cl
H
H
Cl

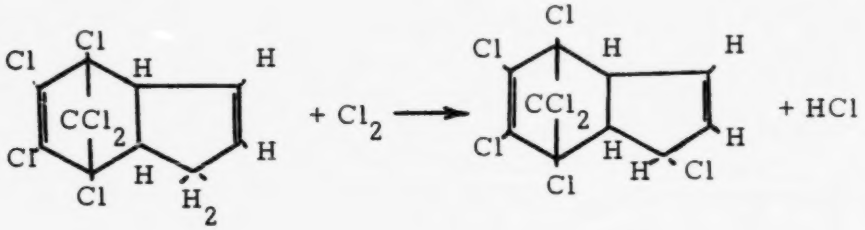
Chlordane (1,2,4,5,6,7,8,8-octachlor-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene) is produced by the reaction of hexachlorocyclopentadiene and chloropentadiene according to the Diels-Alder condensation at atmospheric pressure and 70-85°C:


H
H
H
H
H2
+
Cl
Cl
Cl
Cl
Cl2
Cl
Cl
H
H
CCl2
Cl
H
H
Cl
H2

Chlorination of chlordene produces chlordane:



Heptachlor may be formed by chlorination of chlordene in a benzene solution, resulting in substitution chlorination rather than addition chlorination:



A typical waste stream from a diolefin based chlorinated hydrocarbon pesticide manufacture will include:

COD	500 mg/l
BOD_5	50
Total Solids	1,000
Suspended Solids	100
pH	2
Chlorides	High
Nitrates	?
Phosphates	?
Product	100-300 ppb as Endrin
Toxicity	High
Flow	0.375 gallons treated wastewater/#product

(This does not include concentrated liquids, tank "bottoms", spent catalysts, etc., which are normally landfilled.)

CHAPTER V

PESTICIDAL WASTE TREATMENT TECHNIQUES: REMOVAL, DETOXIFICATION, DEGRADATION, and DECOMPOSITION

This chapter is included to provide a summary of the information contained in the technical literature which deals with the treatment and disposal of pesticides and pesticide wastes. The amount of work reported on this subject is limited and many studies are incomplete. However, all available data were evaluated and are included in as usable form as possible.

Chemistry of Pesticides

Natural insecticides such as rotenone and pyrethrins (plant extracts) are susceptible to hydrolysis, oxidation, and photodegradation. Rotenone is readily detoxified by the action of light and air. Deterioration also takes place with heat (at 100°C, 76% of the rotenone is lost in 2 hours and at 40° C, 4.6% is lost in 30 hours). Pyrethrins are easily hydrolyzed in a basic medium to nontoxic products (Frear, 1955).

Carbamates such as carbaryl (Sevin) are susceptible to hydrolysis in alkaline media. The reaction is rapid at pH levels of 9 or more. The product of alkaline hydrolysis is naphtol. For disposing of small volumes of carbaryl suspended in water, caustic treatment in settling tank may be sufficient. For each 5 pounds of carbaryl actually carried into the tank, addition of 2 pounds of flake caustic will provide a 50% excess of the minimum required to react with the carbaryl. (Flack, 1966 and Anon., Natl. Agr. Chem. Assn., 1965).

Organophosphorus insecticides such as TEPP (tetraethyl pyrophosphate) and parathion are susceptible to hydrolysis. Parathion hydrolysis is accelerated in an alkaline media. Malathion can be hydrolyzed and oxidized. The decomposition is catalyzed by iron salts. Hydrolysis is faster under alkaline conditions. This is illustrated by the following pH study: at a pH of 12, malathion is hydrolyzed almost instantaneously, at pH of 9, 50% is hydrolyzed in about 12 hours and no hydrolysis occurs at pH 5-7 in 12 days (Whitehouse, 1967). In water solutions TEPP is rapidly hydrolyzed even in the absence of alkali. At 25°C the half-life of the compound in neutral water is 6.8 hours and at 38°C it is 3.3 hours. The presence of alkalis also increases their hydrolysis rate greatly. The product of hydrolysis is diethyl phosphoric acid which is non-toxic.

Chlordane in the presence of an alkali dehydrochlorinates to form nontoxic products; this reaction is catalyzed by traces of iron and some other metals (Whitehouse, 1967).

Heptachlor is not affected by acid or alkaline condition and is stable against hydrolysis; however, it is subject to catalytic decomposition by metals such as iron.

Aldrin is stable chemically and is not decomposed by alkaline materials (Whitehouse, 1967). Aldrin in aqueous solutions is readily oxidized by chlorination, potassium permanganate, ozone and aeration; peroxides have no measurable effects. Catalytic decomposition of aldrin results when it is mixed with inert diluents for dusts (Fleck, 1966, Frear, 1955, Buescher, et al., 1964, and Whitehouse, 1967). If oxidation is used, care must be taken to insure complete reaction. The first step in the oxidation of aldrin leads to dieldrin rather than to a nontoxic product Like heptachlor, aldrin is subject to catalytic decomposition if active metals are present.

Dieldrin, like aldrin, is chemically stable and is not decomposed by alkalis and mineral acids; however, it is subject to catalytic decomposition (Frear, 1955).

Isodrin (a stereoisomer of aldrin) is slowly decomposed when heated above 100°C. Like aldrin, isodrin is not decomposed by alkalis (Frear, 1955).

Endrin is not decomposed by alkalis, but acids cause a rearrangement into a compound which does not demonstrate insecticidal activity.

Toxaphene is dehydrochlorinated by heat (at temperatures above 155°C), UV light, and alkalis.

Benzene Hexachloride (BHC) - The isomers of BHC are stable to light, heat, air, carbon dioxide, and strong acids (Whitehouse, 1967). In the presence of alkalis the alpha, gamma, delta, and epsilon isomers are readily dehydrohalogenated. The beta isomer is decomposed slowly by alkali at room temperature, but it is readily broken down at higher temperatures under the same conditions. Approximate second order rate constants for dehydrochlorination at 20°C are (Cristol, 1947):

k_1 (alpha-isomer) = 0.169 liters sec^{-1} mole^{-1}

k_1 (beta-isomer) = 3×10^{-6} "

k_1 (gamma-isomer) = 0.045 "

k_2 (delta-isomer) = 0.110 "

k_3 not determined

where

$$C_6H_6Cl_6 + OH^- \quad {}^{k_1} \quad C_6H_6Cl_5 + H_2O + Cl^-$$

$$C_6H_5Cl_5 + OH^- \quad {}^{k_2} \quad C_6H_4Cl_4 + H_2O + Cl^-$$

$$C_6H_4Cl_4 + OH^- \quad {}^{k_3} \quad C_6H_3Cl_3 + H_2O + Cl^-$$

DDT- In the presence of alkali DDT is dehydrochlorinated to form dehydrochloro-DDT (1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene). This reaction is readily catalyzed by traces of iron, aluminum, and chromium salts. Pure DDT is quite stable in the presence of heat and does not decompose below 195°C, but the technical material decomposes at about 100°C due to the presence of impurities such as iron. The products of thermal decomposition are not pesticidal. DDT is also decomposed by UV light and some investigations have revealed considerable decomposition by exposure to sunlight. DDT in solvents containing chloro- and nitro-groups, such as mono- and dichlorobenzenes, ethylene chloride, and nitrobenzene, is readily decomposed by these materials. DDT is also decomposed by basic organic compounds such as methylamine and dimethylamine(Anon., Chem. Engr., 1969, Mrak, et al., 1969). DDT, however is not subject to hydrolysis since it is almost completely insoluble in water.

TDE or DDD - Its physical and chemical properties are similar to those of DDT. It is dehydrochlorinated in alkali at a slower rate than DDT. It is not affected by exposure to UV under conditions which decomposed DDT, but it is dehydrochlorinated in the presence of ferric chloride at 300°C.

Methoxychlor has generally the same physical and chemical properties of DDT, but it is somewhat more resistant to decomposition in the presence of alkalis. It slowly dehydrochlorinates in strong alkalis.

DFDT - Like DDT, it is easily dehydrochlorinated by alkali.

O, p'-DDT - It is dehydrochlorinated by alcoholic alkali like the p, p' isomer, but at a much slower rate (Frear, 1955).

Dilan - Like DDT, this compound is unstable in the presence of alkalis. It is also oxidized rather easily (Frear, 1955).

Chlorobenzilate - Being an ester, it is decomposed by strong acids and alkalis (Frear, 1955).

Aramite - Being an ester, the material is readily decomposed by alkalis. It is also slowly decomposed by sunlight.

Phenolic herbicides may be oxidized with Fenton's reagent (hydrogen peroxide and ferrous ammonium sulfate catalyst: $Fe(NH_4)_2(SO_4)_2$) and with hypochlorite (chlorine oxidation). Fenton's reagent oxidizes phenol optimally when one mole of ferrous salt and three moles of hydrogen peroxide per mole of phenol are used. Aeration increases the reaction rate and drives the reaction further to completion. Phenolic herbicides, which are substituted phenols, may be oxidized with Fenton's reagent (the greater the degree of substitution, the slower the reaction rate). PCP (pentachlorophenol) is not oxidized by Fenton's reagent. Oxidation with hypochlorite works for phenol and may work for substituted phenols (Eisenhauer, 1964). The chemistry of these compounds is similar to that of an intermediate strength organic acid. They readily form the esters, amides and salts under proper conditions. They also form relatively water-insoluble salts of divalent cations. Strong solutions of acid, amine and other salts of 2,4-D and 2,4,5-T can be precipitated with calcium or magnesium salts to reduce the quantity of pesticides in a gross manner (Fleck, 1966).

Treatment Methods

Chemical Oxidation

Several studies have been conducted on the effects of oxidants on pesticides (Robeck, *et al.*, 1965, Aly and Faust, 1965, Bueschler, *et al.*, 1964, Brower, undated. Cohen, et al., 1960). The following are lists of oxidants commonly used, pesticides tested, and some results of the studies.

Oxidants: Chlorine (Cl_2); chloride dioxide, potassium permanganate ($KMnO_4$); ozone (O_3); and peroxide (H_2O_2, Na_2O_2).

Pesticides: DDT; lindane; parathion; dieldrin; 2,4,5-T ester; endrin; aldrin; rotenone; toxaphene; powdered cube root; sulfoxide; 2,4-DCP; and 2,4-D compounds (sodium salt and esters).

Results:

1) Parathion is oxidized by chlorine and ozone to a more toxic product which is known as paraoxone (Robeck, et al., 1965).

2) 2,4-DCP (parent compound of 2,4-D) is readily oxidized by potassium permanganate (see Figure 3) (Aly and Faust, 1965).

3) In general, unsaturated organic compounds are more susceptible to ozone oxidation than saturated compounds. Buescher, et al. (1964) found that lindane in aqueous solution is readily decreased by ozonation and only partially affected by potassium permanganate. Treatment with chlorination, peroxides, and aeration has no measurable effects (see Table 7, Figure 4, and Figure 5).

4) Aldrin in aqueous solution is readily attached by chlorination, potassium permanganate, ozone and aeration (see Figure 6 and Table 8); peroxides have no measurable effect (Buescher, et al., 1964). According to Brower (Sc.D. Dissertation, 1967), the ozonation products of aldrin are less toxic than aldrin itself.

5) Dieldrin concentration in aqueous solution is decreased by aeration as shown in Figure 7 (Buescher, et al., 1964).

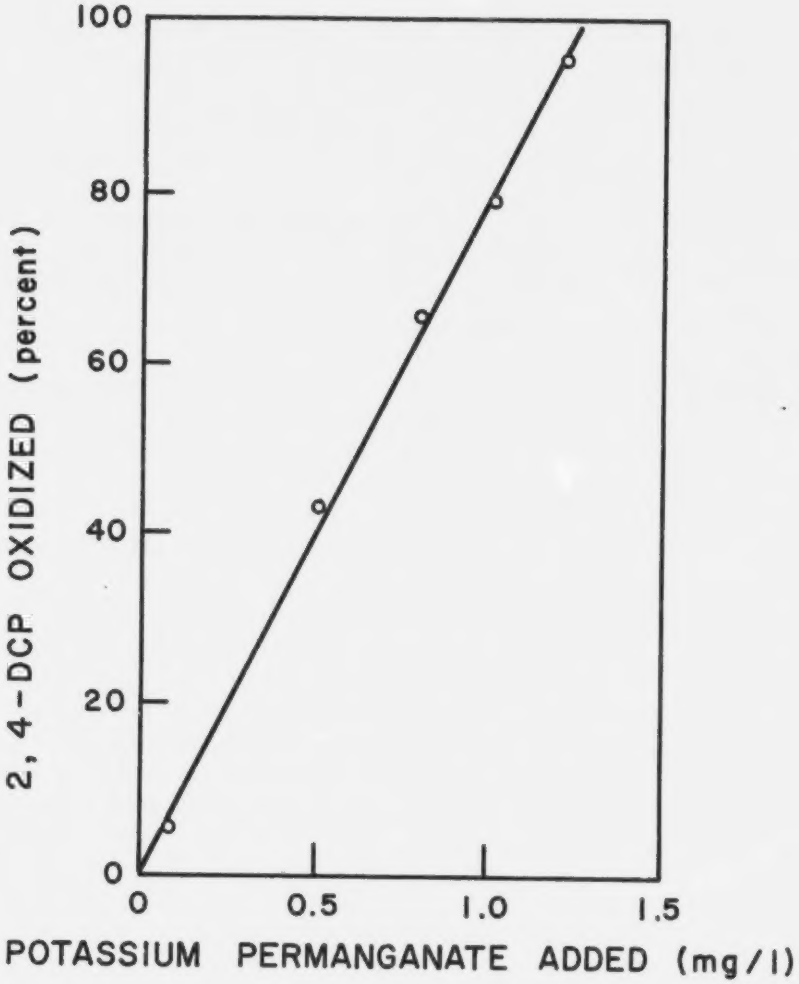


Figure 3. Oxidation of 2,4-DCP with Potassium Permanganate

One-liter solutions of 0.98 mg/l of 2,4-DCP in a phosphate buffer at pH 7.0 were treated with increasing amounts of the oxidant at room temperature. Residual concentration of the phenol was determined at 15 min. As the curve shows, 1.25 mg/l of the oxidant was required for complete oxidation of 1 mg/l of the phenol.

Source: Aly and Faust, 1965.

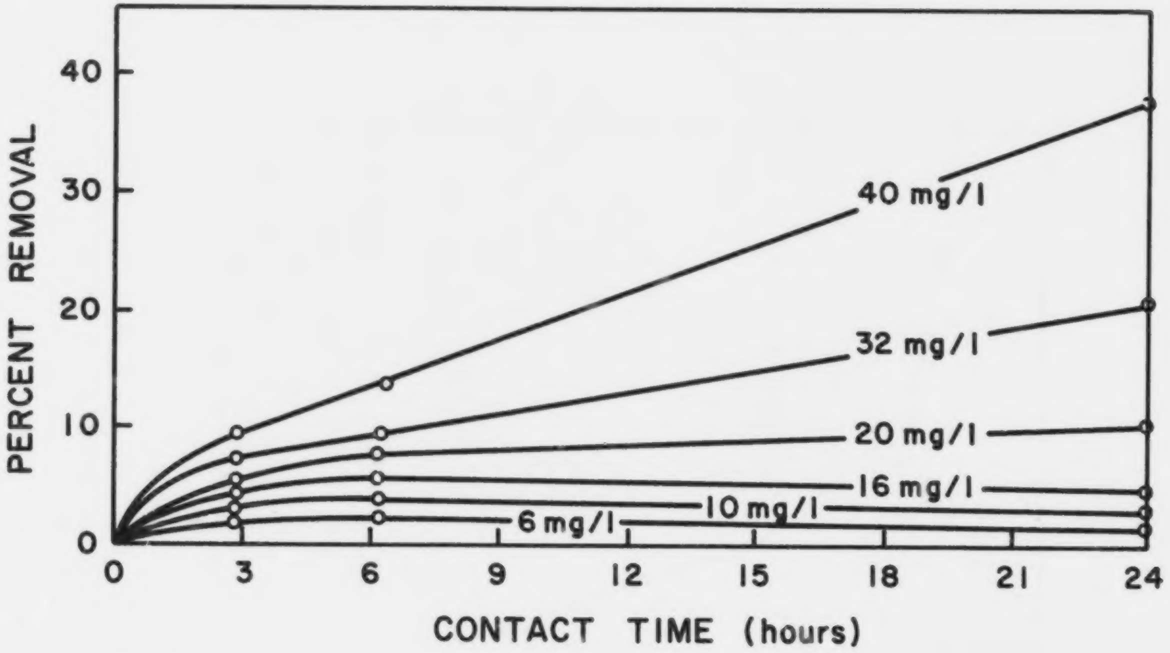


Figure 4. Removal of lindane by treatment with potassium permanganate. The initial concentration was approximately 8 mg/l lindane in distilled water. Lines and values represent the concentration of $KMnO_4$ added.

Source: Buescher, _et al_., 1964.

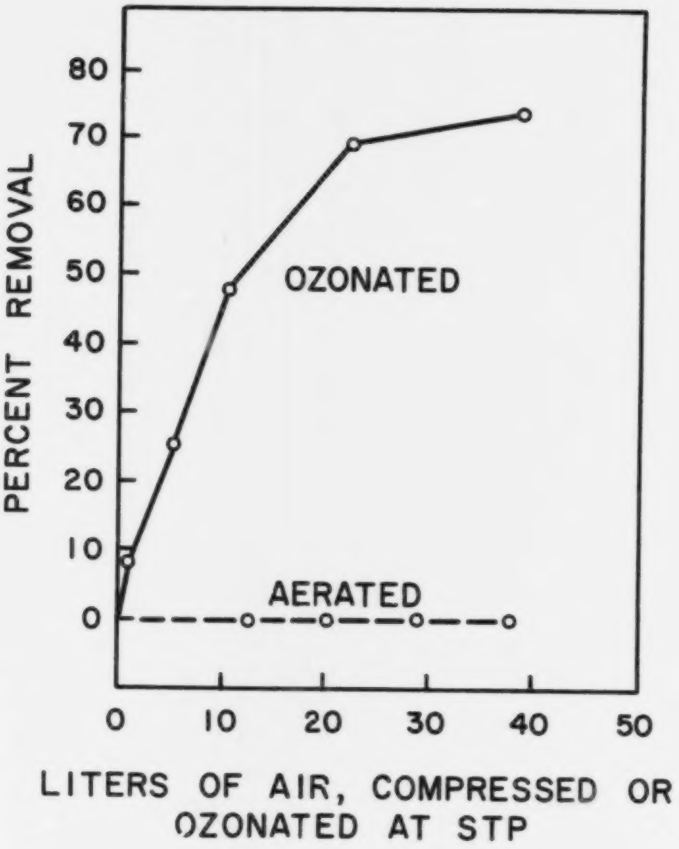


Figure 5. Removal of lindane by aeration and ozonation. The initial concentration of lindane was approximately 8 mg/l in distilled water. The ozone concentration was 3.9% by weight in air injected at a rate of 0.3 l/m through a 2.5 l reactor. 10% ozone absorption was achieved.

Source: Buescher, et al., 1964.

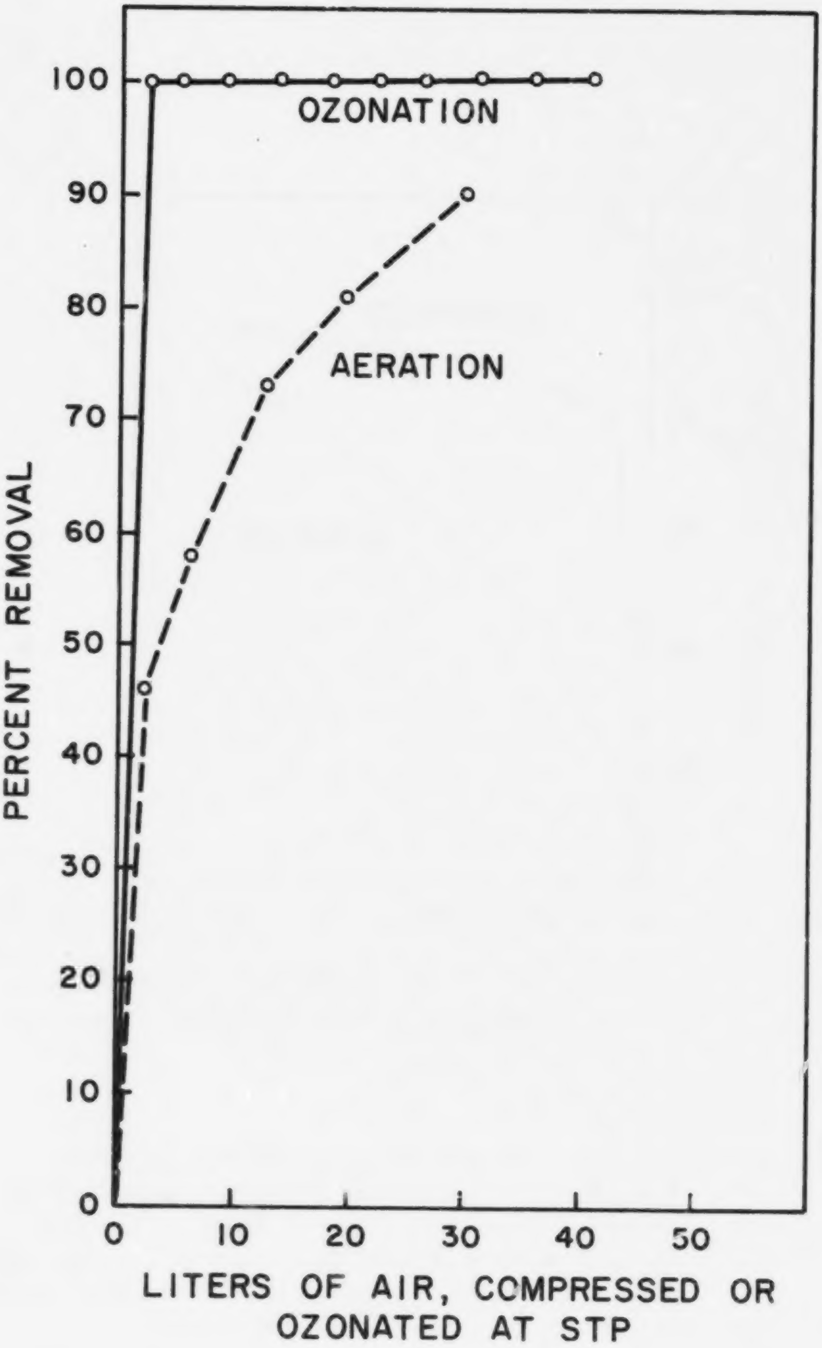


Figure 6. Removal of aldrin by aeration and ozonation. The initial concentration of aldrin was approximately .02 mg/l in distilled water. The ozone concentration was 3.9% by weight in air injected at a rate of 0.3 l/m through a 2.5 l reactor. 10% ozone absorption was achieved.

Source: Buescher, et al., 1964.

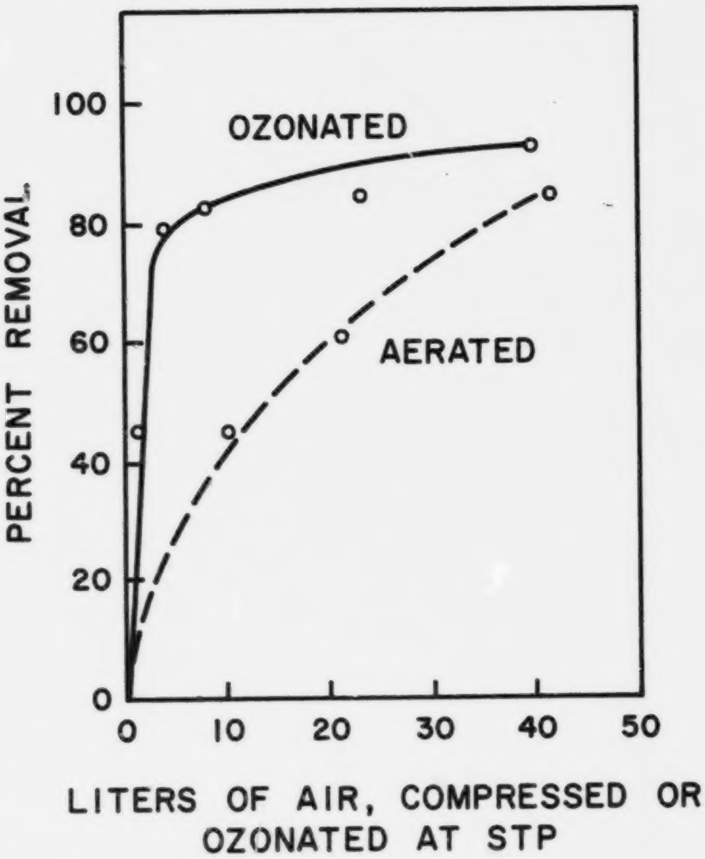


Figure 7. Removal of dieldrin by aeration and ozonation. The initial concentration of dieldrin was approximately 0.2 mg/l in distilled water. The ozone concentration was 3.9% by weight in air injected at a rate of 0.3 l/m through a 2.5 l reactor. 10% ozone absorption was achieved.

Source: Buescher, et al., 1964.

Table 8. Effects of Oxidants on Pesticides in Aqueous Solution[13]

Oxidant	Oxidant Dosage (mg/l)	Pesticide Studied	
		Lindane	Aldrin
Cl_2	40	Negligible	Positive
H_2O_2	40	Negligible	Negligible
Na_2O_2	40	Negligible	Negligible
$KMnO_4$	40	Positive	Positive
Ozone	3.9% by wt. of ozonized air at 0.3 l/m	Positive	Positive

Source: Buescher, et al. (1964)

6) Rotenone and rotenoid compounds; Cohen, et al. (1960) state that chlorine and chlorine dioxide are effective against these compounds, but some means must be provided for removing the substantial amount of residual chlorine as shown in Figures 8 and 9.

Coagulation

Alum coagulation studies by Robeck, et al. (1965), Cohen, et al. (1960), and Whitehouse (1967) have been conducted on several pesticides. The following is a list of pesticides studied and some results of the studies.

Pesticides: DDT; Lindane; Parathion; Aldrin; Dieldrin; Captan, BHC; Malathion; and fish poisons (rotenone, toxaphene, cube root, sulfoxide).

Results:

1) DDT is easily removed by alum coagulation at doses typical of conventional water treatment. Efficiencies of removal are 98% for a 10 ppb load and 97% for a 25 ppb load (Robeck, et al., 1965).

2) Lindane and parathion have low efficiencies of removal by conventional alum coagulation and sand filtration. For a load of 10 ppb, the removal efficiency is 10% for lindane and 20% for parathion (Robeck, et al., 1965).

3) Fish poisons (rotenone, toxaphene, cube powder, and commercial formulations) are not removed by alum coagulation. Treatment of these compounds with as much as 100 mg/l alum produces no significant reduction in concentration (0.1 mg/l initial concentration of rotenone and toxaphene; 2.0 mg/l initial concentration of cube powder and commercial formulations) (Cohen, et al., 1960).

4) Aldrin, Dieldrin, Captan, BHC, and Malathion have low efficiencies of removal by chemical coagulation. Aldrin (0.2 mg/l), Dieldrin (.05 mg/l), Captan (.556 mg/l), and BHC (.0178 mg/l)

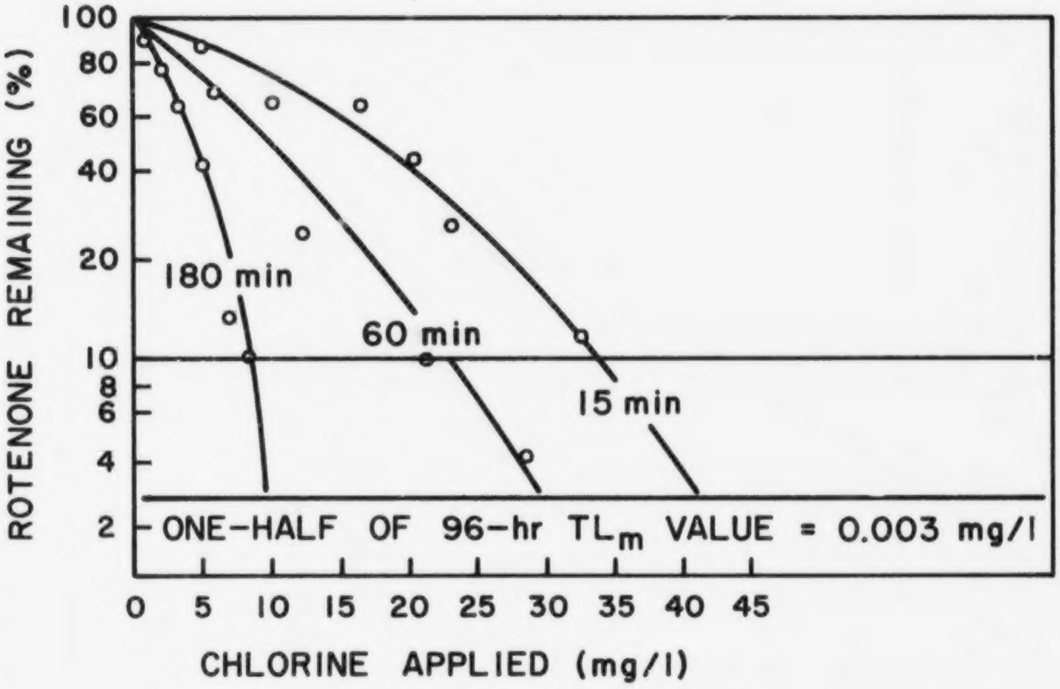


Figure 8. Effectiveness of Chlorine Treatment of 0.1 mg/l Rotenone Solution

The data in Table 5 have been plotted to provide, by extrapolation, an estimation of the amount of chlorine required to reduce the toxicity of 0.1 mg/l rotenone to one-half the 96-hr TL_m (median tolerance limit).

Source: Cohen, et al., 1960.

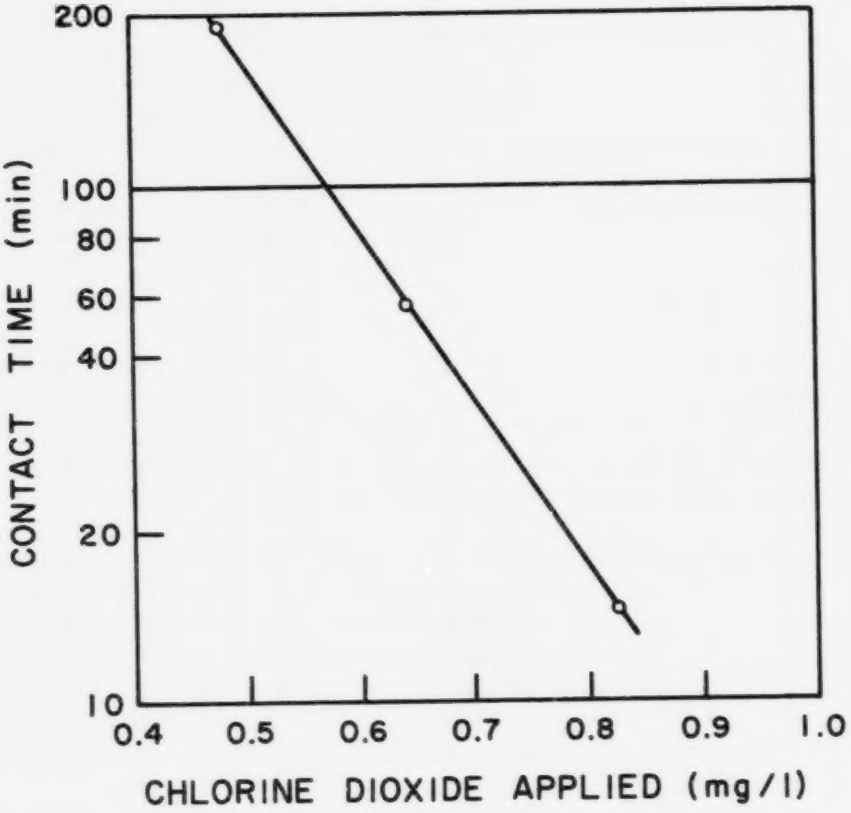


Figure 9. Contact Time and Chlorine Dioxide Required to Detoxify 0.1 mg/l Rotenone.

The temperature of the solution was 25°C; the pH, 7.5.

Source: Cohen, et al., 1960.

were treated with alum (Aluminum sulfate, 0.02 to 1.0 grams per liter). The hardness of the samples was 10, 100, and 250 mg/l ($CaCO_3$). The percent removal was approximately 6% for Aldrin, 13% for Dieldrin, 3% for BHC, and 2% for Captan. Neither the alum dosage nor the hardness variation seems to affect the removal to any great extent. Malathion (100 to 180 mg/l) was treated with alum, ferric sulfate (72% $Fe_2(SO_4)_3$), and alum plus coagulant aids. The percent removal was approximately 10% for an alum dosage of 250 mg/l. Ferric sulfate removed about 10% of the malathion for a dosage of 400 mg/l. Coagulant aids had little effect upon alum removal of malathion.

Adsorption

Many adsorption studies (Robeck, et al., 1965, Aly and Faust, 1965, Cohen, et al., 1960, Whitehouse, 1967, Sigworth, 1965, Coffey, 1967, Faust and Suffet, 1966, MacNamara, 1968) have been conducted on a large number of pesticides. The following are a list of adsorbents used, a list of pesticides studied, and some results of the studies.

Adsorbents: Activated carbon; saturated clay systems (H/Al, Ca Mg, K); humic acid, New Jersey soils, muck soil (organic soil); bentonite clay; cation exchange resin; anion exchange resin; EPK (Edgar Plastic Kaolin from the EPK Company); hydrous aluminum silicate; USP (Fisher Scientific Company); and Diluex (hydrous magnesium aluminum silicate).

Pesticides: DDT, DDD; lindane; parathion; dieldrin; endrin; aldrin; chlordane; malathion; captan; BHC; 2,4-D derivatives; 2,4-DCP; 2,4,5-T ester; toxaphene; rotenone; CIPC; DCPA; DNBP; trifluralin; diphenamide; amiben; paraquat; and linuron.

Results of studies on activated carbon:

1) Activated carbon studies on herbicides and pesticides (Sigworth, 1965) have shown that

it is successful in reducing the concentration of these toxic compounds. Investigations have included such widely used herbicides and insecticides as BHC, DDT, 2,4-D, toxaphene, dieldrin, aldrin, chlordane, malathion, and parathion (see Table 9).

2) Activated carbon studies on the removal of fish poisons (Cohen, et al., 1960) have shown that rotenone, toxaphene, and the solvents and emulsifiers present in all the commercial fish poison formulations are removed. This broad activity also eliminates odors.

3) A study by Whitehouse (1967) on the removal of malathion, 2,4-D, aldrin, dieldrin, and DDT (by means of adsorption on activated carbon) showed that substantially 100% removal could be obtained for all levels of pesticide used.

4) Activated carbon adsorption studies on herbicides have shown that the amount of adsorption as measured by the reduction in biological activity was as follows:

   CIPA >trifluralin > 2,4-D > diphenamide >DCPA > DNBP > amiben (Coffey, 1967). CIPC and trifluralin which were the most readily adsorbed by activated carbon were desorbed the least. 2,4-D was readily desorbed from both activated carbon and bentonite clay.

5) Table 9 shows that activated carbon easily removes DDT, lindane, parathion, dieldrin, endrin, and 2,4,5-T ester (for initial concentrations of 10 ppb).

6) Table 10 shows high efficiency of adsorption for BHC, chlordane, DDT, aldrin, DDD, and endrin.

7) Table 11 gives the effects of activated carbon on parathion, BHC, malathion, 2,4-D, chlordane, and DDT.

Table 9. Summary of Cumulative Pesticide Removal at 10-ppb Load from Raw River Water

Process	Pesticide Removed--per cent					
	DDT	Lindane	Parathion	Dieldrin	2,4,5-T Ester	Endrin
Chlorination--5ppm chlorine (Batch test-90 minute contact)	<10	<10	75*	<10	<10	<10
Alum coagulation and sand filtration	98	<10	80**	55	65***	35
Carbon:						
Slurry - Slow mixing						
5 ppm ($2x10^{-3}$ #/# carbon)		30	>99	75	80	80
10 ppm ($1x10^{-3}$ #/# carbon)		55	>99	85	90	90
20 ppm ($5x10^{-4}$ #/# carbon)		80	>99	92	95	94
Bed--0.5 gpm/cu.ft. of carbon	>99	>99	>99	>99	>99	>99

*Oxidized to paraoxon, which is more toxic than parathion.

**A value of 20% is reported by Robeck, et al., 1965.

***A value of 63% is reported by Robeck, et al., 1965.

Source: Robeck, et al., 1965.

Table 10. Efficiency of Adsorption and Recovery from Carbon

Insecticide	Percent Adsorbed	Percent Recovered
BHC	99	80
Chlordane	99	75
DDT	98-100	76
Aldrin	97	85
DDD	96-100	82
Endrin	91	86

BHC - 8 liters of 5 ppm emulsion were passed through 12 grams of carbon.
Chlordane - 8 liters of 5 ppm emulsion were passed through 12 grams of carbon.
DDT - 200 liters of 2.5 ppm emulsion were passed through 30 grams of carbon.
Aldrin, DDD, Endrin - No data reported.

Source: Faust and Suffet, 1966.

Table 11. Effect of Activated Carbon on Herbicides and Insecticides

Pesticide	Concn. Treated With Carbon (ppm)	Carbon Dosage Used (ppm)	Threshold Odor Values		Threshold Odor Units Removed per ppm Carbon	Concn. After Treatment	
			Before	After		Calcd. From Odor Reduction (Units)	Detd. by Chemical Anal. (ppm)
Parathion	10	10	50	4	4.6	0.8	2.6
BHC-37, gamma	25	5	70	6	12.6	0.22	0.08
Malathion, 50 per cent	2	10	50	4	4.6	0.08	0.25
2,4-D, 23.5 per cent	6	20	50	3	2.4	0.085	1.38
2,4-D, 11.7 per cent	1	10	70	2	6.8	0.005	L*
Chlordane, 6 per cent	50	10	50	1.4	4.9	0.084	L*
DDT, 50 per cent	5	2	70	4	33	0.15	L*

*Concentrations were to low to determine by available test methods.

Source: Sigworth, 1965

8) Tables 12 and 13 give the carbon dosages required to reduce the concentrations of 2,4-D compounds and 2,4-DCP (the parent compound of 2,4-D). Various amounts of the carbon (activated) were added to 1 liter volumes of fixed concentrations of the sodium salt and the isopropyl, butyl, and isooctyl esters of 2,4-D and 2,4-DCP. These suspensions were stirred rapidly at room temperature $25^{\circ}C \pm 2^{\circ}C$ for 30 minutes. Then the carbon was removed rapidly by vacuum filtration through filter paper. As the data in Table 12 indicates, large carbon dosages are required for good removal, making the process expensive if large volumes of wastewater are involved.

9) Figure 10 gives the carbon dosages required for removal of fish poisons. The final concentration of the poisons desired is half the 96-hour TLM - medium tolerance limit (Cohen, et al., 1960).

10) Figures 11, 12, and 13 show the results of tests of the removal of DDT, aldrin, and dieldrin as a function of contact time. The experimental procedure consisted of placing 200 ml of pesticide mixture into a flask containing 60 mg of activated carbon (300 mg/l). Seven flasks, each containing 300 mg/l of carbon in a pesticide mixture, were then placed on a Burrell wrist action shaker and agitated for specified times of 15 minutes, 30 minutes, 45 minutes, 1 hour, 1.5 hours, 2 hours, and 3 hours. Figures 14, 15, and 16 show the results of tests of the removal of dieldrin, aldrin and DDT as a function carbon dosage (Whitehouse, 1967). The experimental procedure consisted of placing 200 ml of pesticide mixture into flasks which contained a specific concentration of carbon (5 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, 300 mg/l, 500 mg/l, 700 mg/l, or 900 mg/l). The flasks were then placed on the shaker and mixed for the optimum time.

Table 12. Carbon Dosages Required to Reduce the Concentration of 2, 4-D Compounds *

Initial Concn.** (mg/l)	Carbon Dosage (mg/l)			
	Sodium Salt	Isopropyl Ester	Butyl Ester	Isooctyl Ester
10	306	150	165	179
5	153	74	82	89
3	92	44	49	53
1	31	14	15	16

*Final concentration 0.1 mg/l.
**Expressed as the acid equivalent.

Source: Aly and Faust, 1965.

Table 13. Carbon Dosages Required to Reduce the Concentration of 2,4-DCP*

Initial Concn. (μg/l)	Carbon Dosage (mg/l)	# Removed / # Carbon
100	5.9	1.66×10^{-2} **
80	4.7	1.33×10^{-2} **
50	2.9	1.65×10^{-2} **
30	1.7	1.64×10^{-2} **

*Final Concentration 2.0 μg/l.
**Not in original table, calculated by author.

Source: Aly and Faust, 1965.

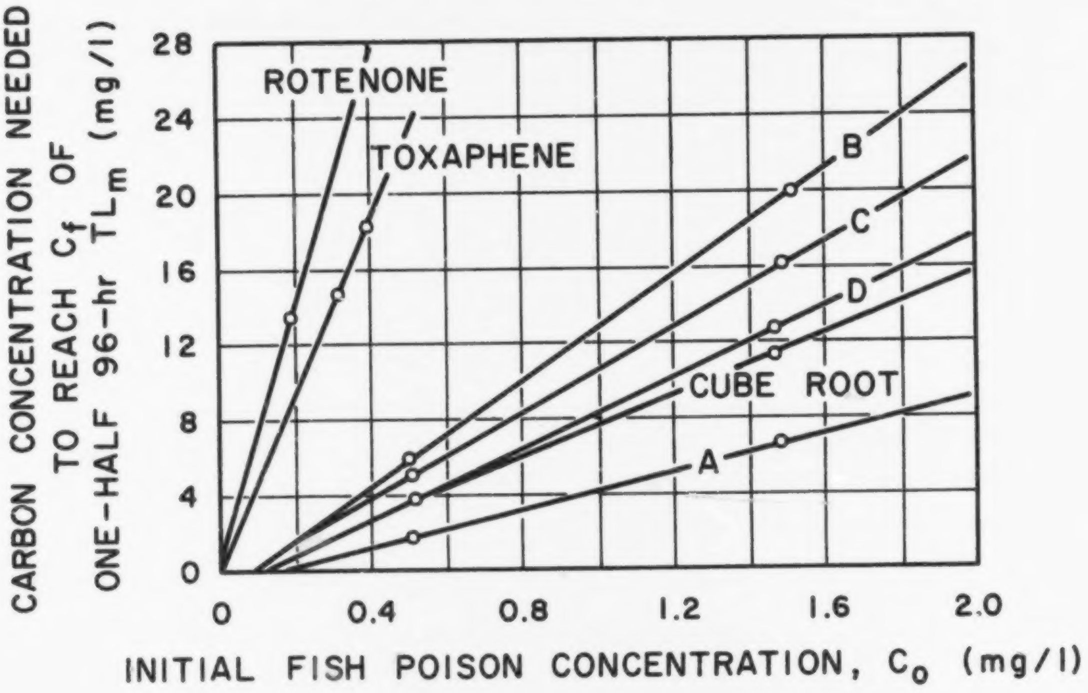


Figure 10. Carbon Dosage Curves for Removal of Fish Poisons

From these curves, the amounts of carbon required to reduce any concentration of fish poison to the selected permissible residual concentration can be determined.

Curves A, B, C, and D refer to the following poison formulations:

Formulation A: active ingredients 2% rotenone and 7% toxaphene

Formulation B: active ingredients 5% rotenone and 15% other cube extractives

Formulation C: active ingredients 2.5% rotenone, 5% cube extractives, and 2.5% sulfoxide

Formulation D: active ingredients 5% rotenone and 10% other cube extractives

Cube root - A fish poison

Source: Cohen, et al., 1960.

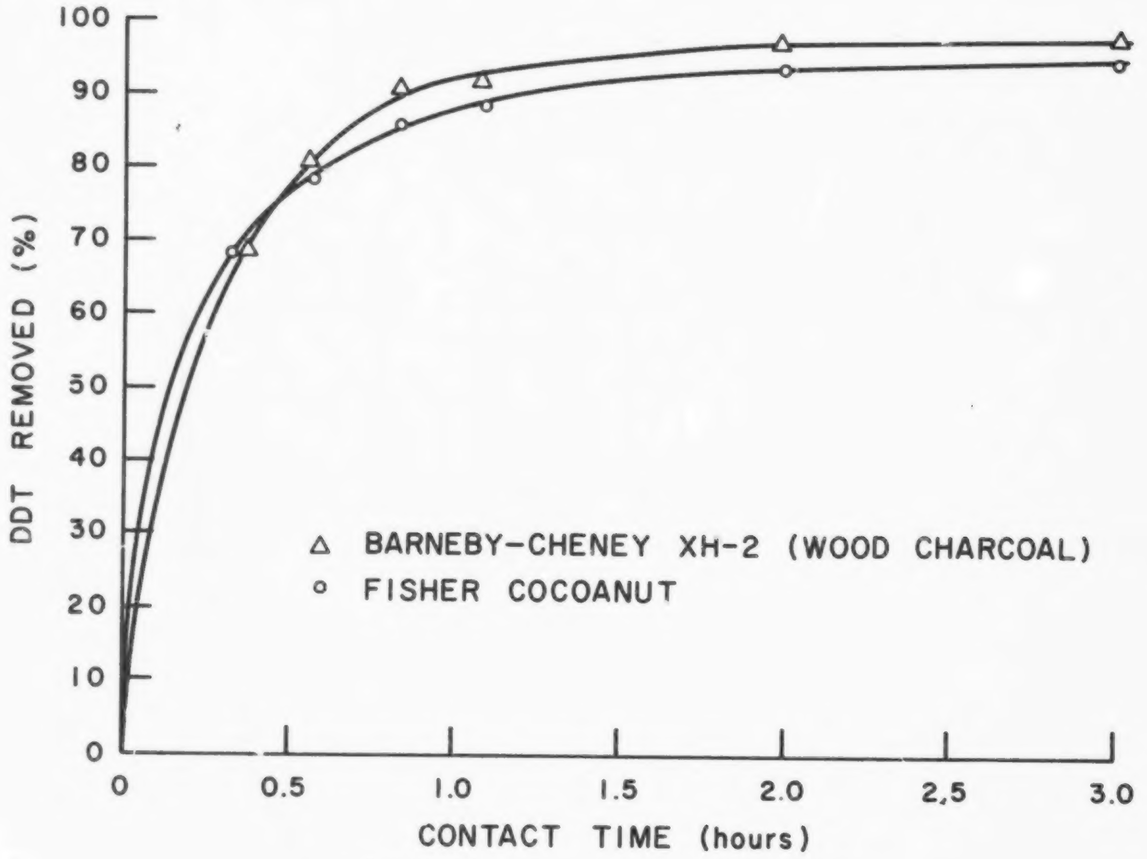


Figure 11. Removal of DDT from Solution
as a Function of Contact Time

Initial DDT Concentration = 0.0044 ppm
Carbon Dosage = 100 ppm
pH = 6

Source: Whitehouse, 1967.

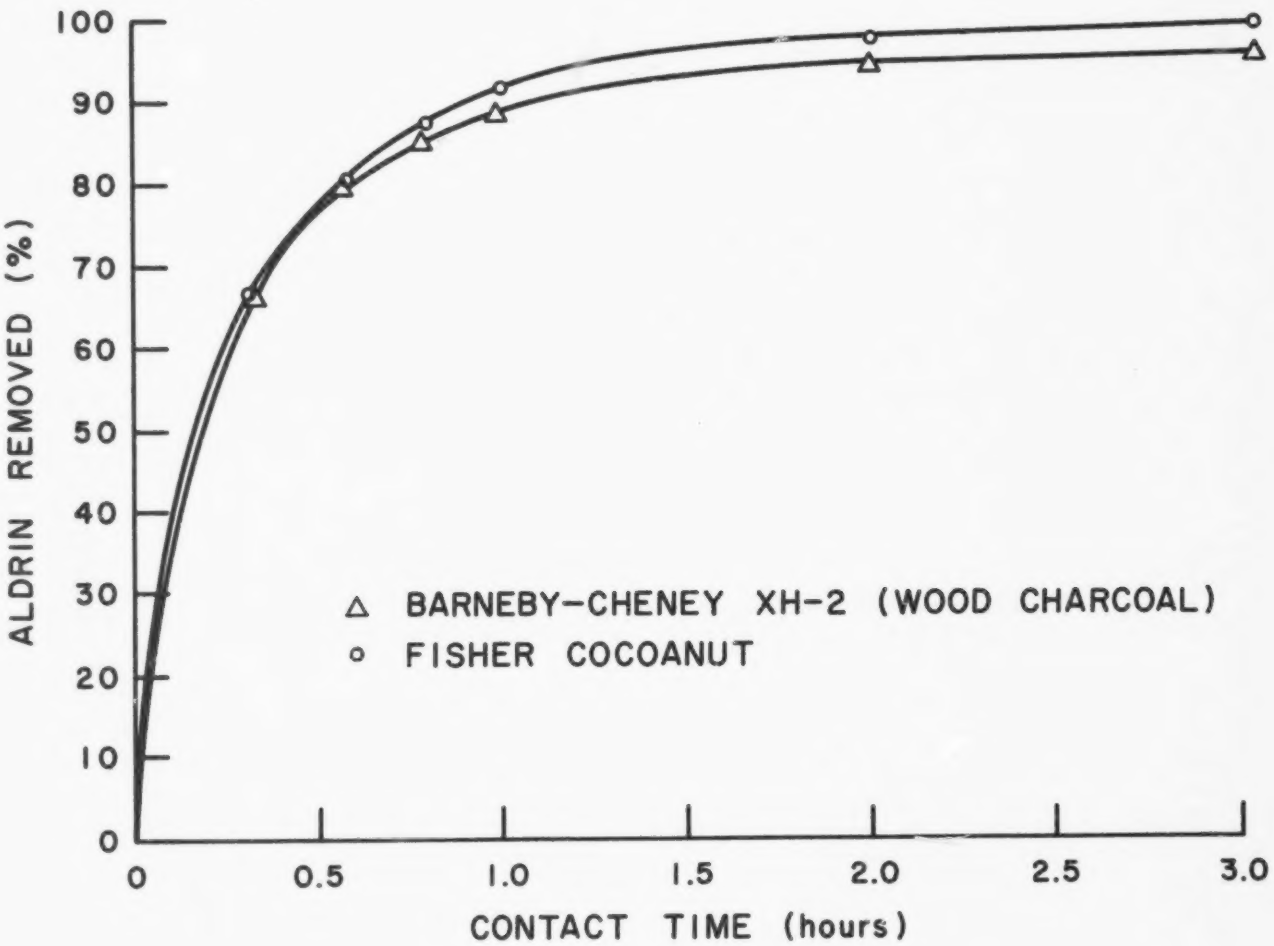


Figure 12. Removal of Aldrin from Solution as a Function of Contact Time

Initial Aldrin Concentration = 0.0066 ppm
Carbon Dosage = 100 ppm
pH = 6

Source: Whitehouse, 1967.

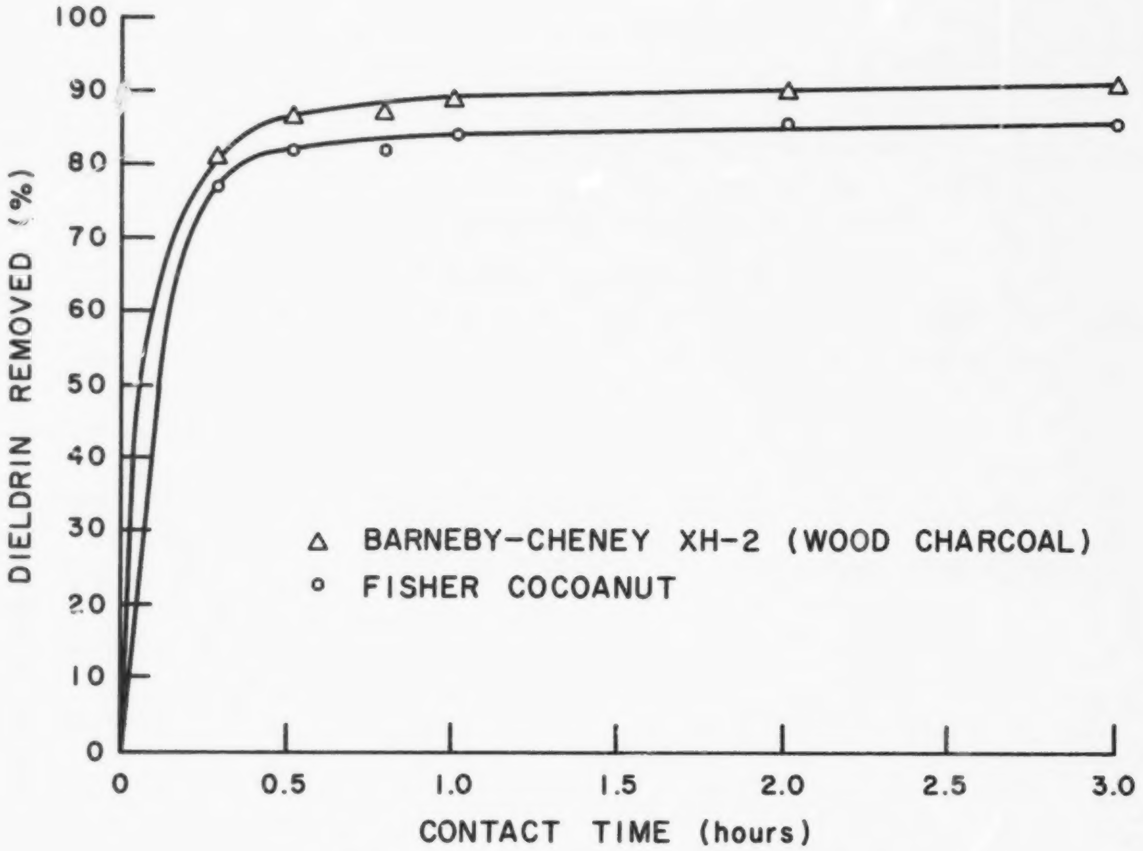


Figure 13. Removal of Dieldrin drom Solution as a Function of Contact Time

Initial Dieldrin Concentration = 0.0040 ppm
Carbon Dosage = 100 ppm
pH = 6

Source: Whitehouse, 1967.

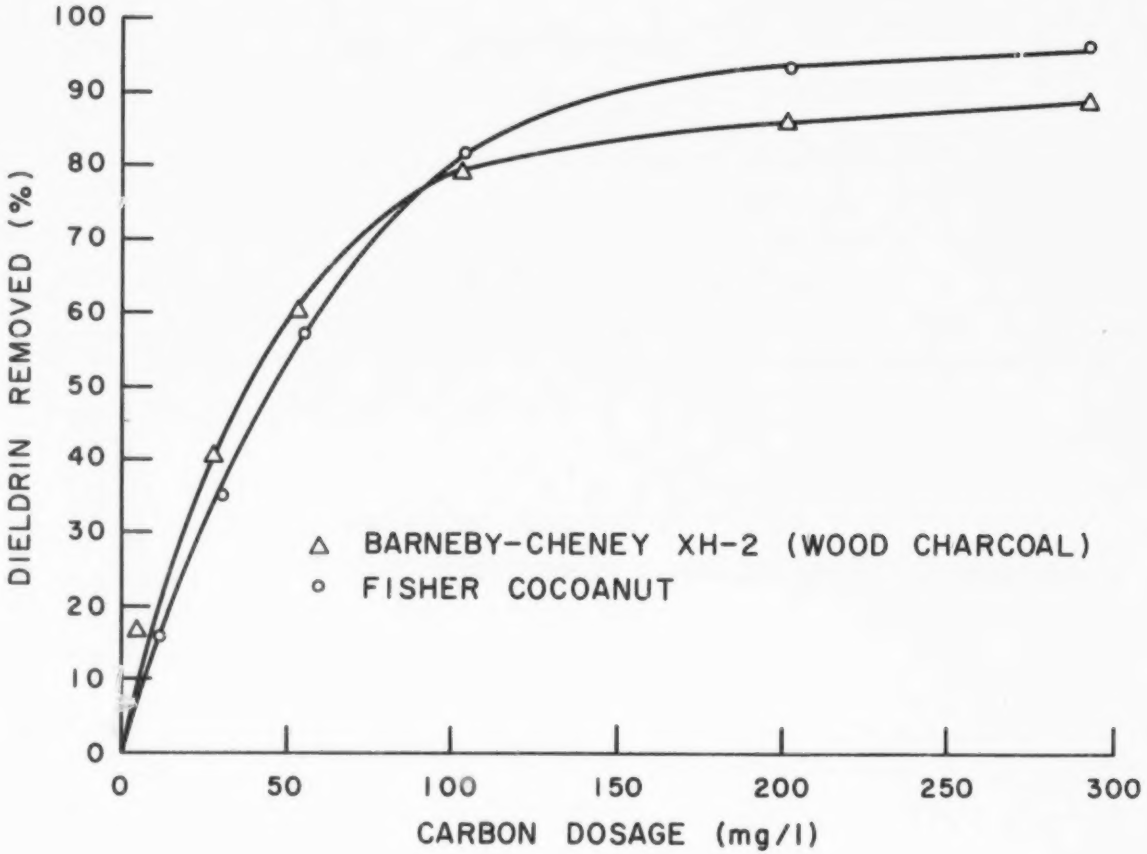


Figure 14. Removal of Dieldrin from Solution
as a Function of Carbon Dosage

Initial Dieldrin Concentration = 0.0040 ppm
Contact Time = 1 Hour
pH = 6

Source: Whitehouse, 1967.

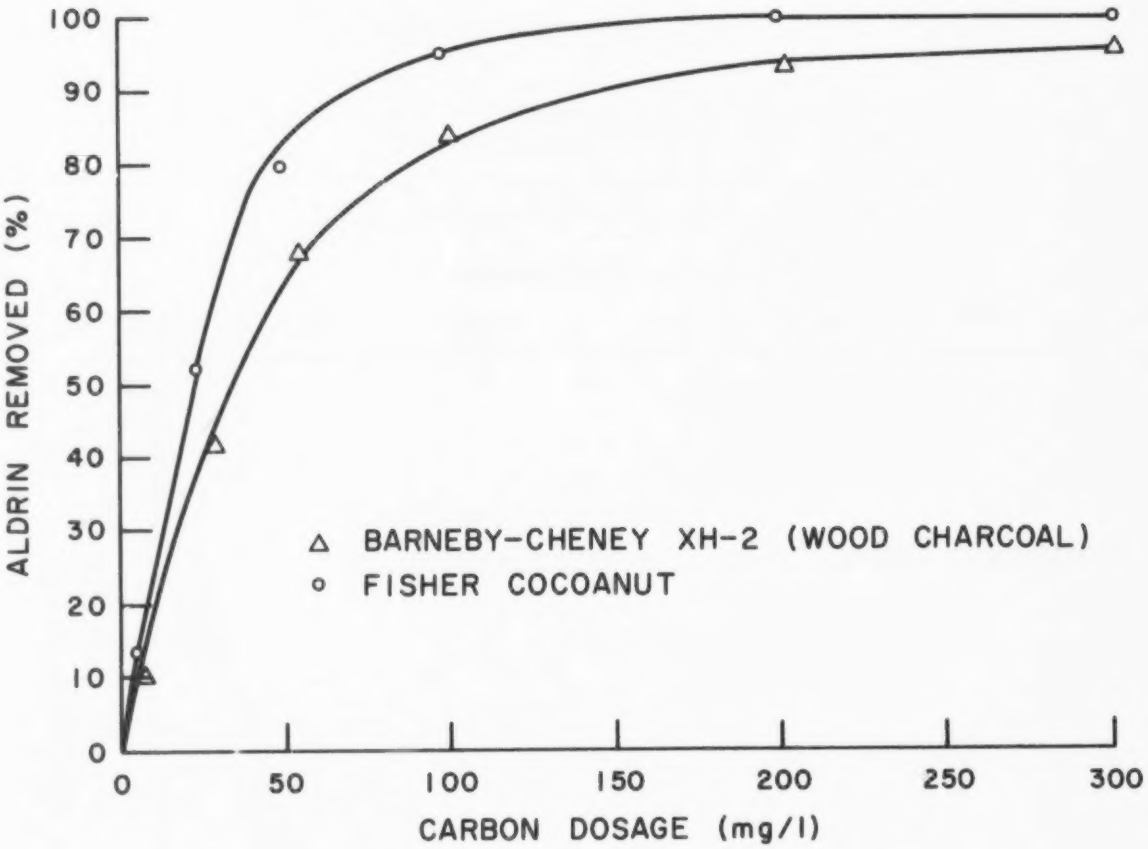


Figure 15. Removal of Aldrin from Solution as a Function of Carbon Dosage

Initial Aldrin Concentration = 0.0066 ppm
Contact Time = 1 Hour
pH = 6

Source: Whitehouse, 1967.

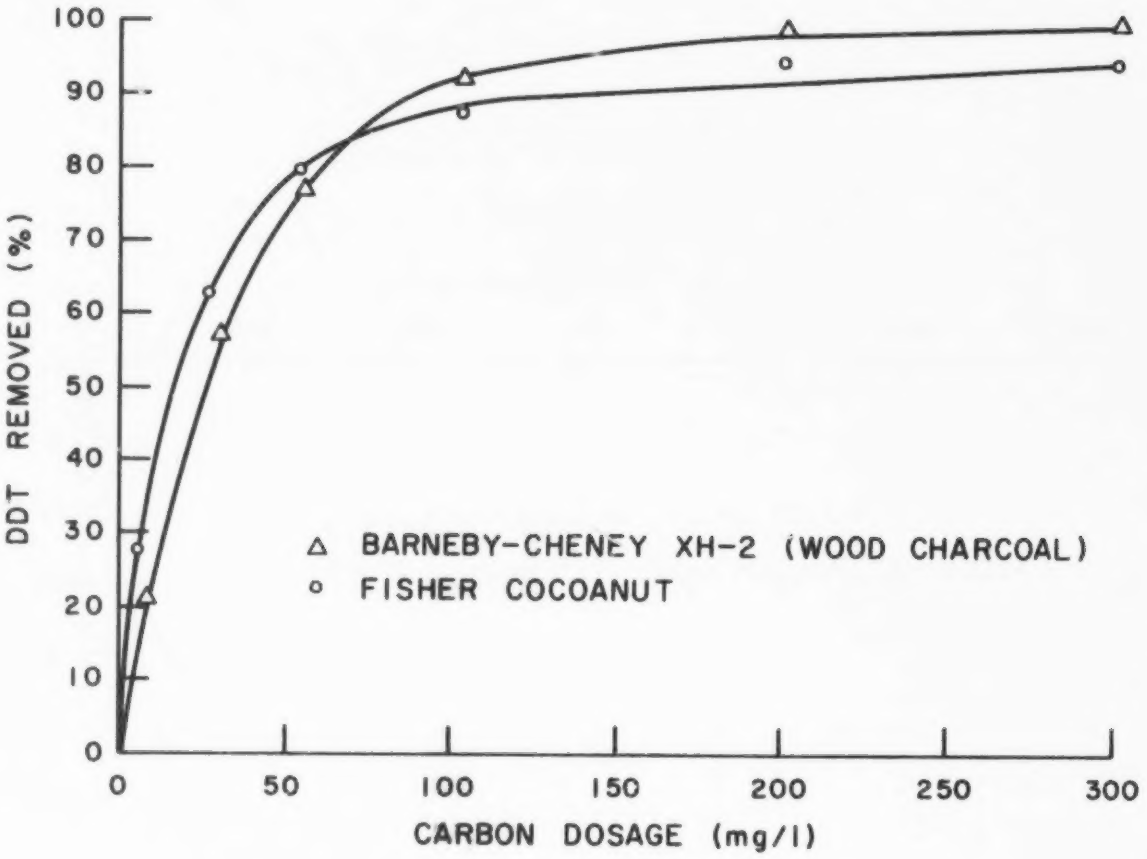


Figure 16. Removal of DDT from Solution as a Function of Carbon Dosage

Initial DDT Concentration = 0.0044 ppm
Contact Time = 1 Hour
pH = 6

Source: Whitehouse, 1967.

Results of studies on clays, resins, and other adsorbents:

1) The adsorption of linuron, malathion, diphenamide and DDT was studied using H/Al, Ca, Mg, and K saturated clay systems and humic acid. Adsorption by homoionic clays and humic acid was in the order of malathion > diphenamide > linuron with the exception of negative adsorption of diphenamide in H/Al and Mg kaolinite and H/Al illite clays. Potassium homoionic clays generally adsorbed more linuron, diphenamide and malathion than did other clay systems. DDT clay systems indicated almost total removal of the insecticide (MacNamara, 1968).

2) An adsorption study of herbicides by Coffey (1967) showed that the biological activity of paraquat, a cationic herbicide, was not reduced by bentonite clay and cation exchange resin. DNBP (4,6-dinitrophenol-O-sec butylphenol) was also shown to be more strongly adsorbed by an anion exchange resin than by activated carbon.

3) An adsorption study by Whitehouse (1967) indicated partial adsorption of aldrin, dieldrin, DDT, 2,4-D, BHC, captan, and 2,4,5-T by clays. The clays used were: EPK - Edgar Plastic Kaolin, hydrous aluminum silicate obtained from the Edgar Plastic Kaolin Company; Bentonite, U.S.P. obtained from the Fisher Scientific Company; and Dilvex, a hydrous magnesium aluminum silicate obtained from the Floridan Company.

4) In an adsorption study with ion-exchange resins, Aly and Faust (1965) showed that strongly basic anion exchange resins can be used for partial removal (about 30 to 40%) of high concentrations of 2,4-D (120 mg/l sodium salt, 10 mg/l Butyl Ester) and 2,4-DCP (10 mg/l) similar to those that may result from the discharge of industrial wastewaters into natural waters.

Photochemical Degradation

Photochemical degradation studies by Bulla and Edgerly (1968), Smith and Grove (1969), and Crosby (undated) have been conducted on several pesticides and pesticide groups. The pesticides and pesticide groups studied included aldrin, dieldrin, endrin, guthion, chlorinated herbicides, carbamates, and diquat. Some results of the studies were:

1) Irradiation by a 2537 Å energy source decreases the toxicity of aldrin to some fish. Figure 17 gives photochemical degradation curves for aldrin, dieldrin and endrin (Bulla and Edgerly, 1968).

2) Smith and Grove (1969) reported that in dilute solution radioactively labeled diquat is rapidly degraded by filtered radiation from a mercury vapor lamp and also by natural sunlight to give identical photochemical decomposition products.

3) UV irradiation of some pesticides and pesticide groups had the following effects as reported by Crosby (1969):

Pesticide (group)	
Dieldrin	Isomerization
Chlorinated compounds	Reduction
Guthion	Reduction
Chlorinated herbicides	Replacement of aromatic halogens by hydroxyl
Carbamates	Elimination

Liquid-Liquid Extraction

An extensive study by Faust and Suffet (1966) was made on liquid-liquid extraction of pesticides with various solvents. Table 14 summarized the results of this study. Most extractions show high percent recoveries. Another study by Shrivastava (1967) on liquid-liquid extraction shows that benzene is very effective in removing DDT from manufacturing wastes.

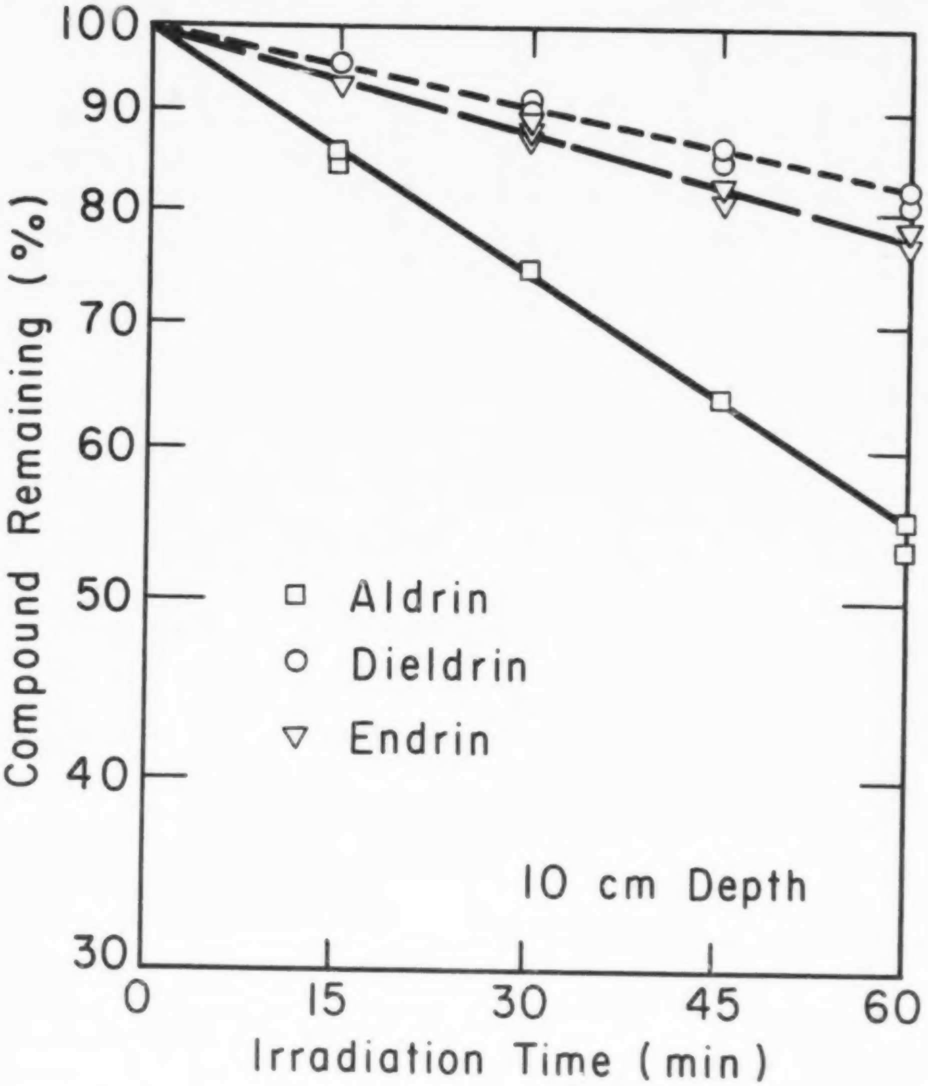


Figure 17. Photochemical Degradation Rates for Aldrin, Dieldrin, and Endrin (2537 Å source).

Source: Bulla and Edgerly (1968)

Table 14. Liquid-liquid Extraction Systems and Percent Recoveries
1:1 Solvent to Aqueous Phase Volume Ratio

Pesticide(s)	Solvent(s)	No. of Extractions	Sample Volume (Liters)	pH	Mean Recovery (%) (Total)	Reference
DDT	3:1 Ether and n-hexane	4	1.5	4.0-5.0	88[a], 61[b]	Berc[illegible]53)
Parathion	1:1 Benzene & n-hexane	Cont.	200	---	97	Sumiki and Matsuyama (1957)
Dieldrin and metabolites	n-hexane	4	0.1	---	90-95	Cueto and Hayes (1962)
DDT, toxaphene, aldrin, dieldrin, BHC	1:1 Ether-pet. ether or $CHCl_3$	5	1.0	---	88	Teasley and Cox (1963)
Parathion and diazinon	1:1 Ether-pet. ether or $CHCl_3$	5	1.0	---	90	Teasley and Cox (1963)
2,4-D, MCPA, 2,4,5-T	$CHCl_3$	3	0.3	2.0	93	Erne (1963)
2,4-D	1:3 Ether and $CHCl_3$	3	0.25	2.0	102[a], 101[c], 99.9[d]	Aly and Faust (1963)
5 Phenoxyalkyl acids, + dalapon	Ether	4	0.1	2.0	96[e]	Abbott *et al.* (1964)

Table 14. (Continued)

Pesticide(s)	Solvent(s)	No. of Extractions	Sample Volume (Liters)	pH	Mean Recovery (%)	Reference
6 Cl_2-hydrocarbons	Pet. ether	Cont.	20	---	97	Kahn and Wayman (1964)
8 Cl_2-hydrocarbons	n-hexane	2	1	---	98	Lamar *et al*. (1965)
Dipterex and DDVP	Ethyl acetate	2	0.05	8.0	94.5	El-Refai and Giuffrida (1965)
2,4-D, dieldrin, perthane	Pet. ether	Cont.	18	---	93, 87, 93	Sanderson and Ceresia (1965)
8 Triazine herbicides	Dichloromethane	2	0.2	9.0	92.5[f]	Abbott *et al*. (1965)
Organophosphates and Cl_2-hydrocarbons	n-hexane	1	1	Acid	90	Warnick and Gaufin (1965)

[a] Interferences absent.
[b] Interferences present.
[c] Interferences present; 2,4-D measured by a colorimetric method.
[d] Interferences present, 2,4-D measured by ultraviolet absorption.
[e] Mean value for the six herbicides.
[f] Mean value for the eight herbicides.

Source: Faust & Suffet, 1966.

Biological Degradation

Biological degradation studies by Stutz (1966), Mills (1959), Randall (1963), Chacko, *et al*. (1966), Matsumura, *et al*. (1967), Loos (1967), Bounds and Colmer (1965), Newland, *et al*. (1969), Hill and McCarty (1967) have been conducted on several pesticides. These studies involve the activated sludge treatment method as well as microbial degradation under aerobic and anaerobic conditions. The following is a list of the pesticides tested, a list of the microbes used, and some results of the studies.

Pesticides: Parathion; methyl parathion; DDT; PCNB; dieldrin; 2,4-D; 2-CPA; 4-CPA; MCPA; silvex; fenac; delapon; CDAA; CIPC; 2,4,5-T; heptachlor epoxide; lindane; haptachlor; endrin; DDD; and aldrin.

Microbes: Actinomycetes; filamentous fungi; soil microorganisms; bacterial enzymes; and streptomyces.

Results:

1) Pilot plant tests made on parathion wastes combined with domestic wastes show that parathion wastes can be treated successfully in municipal activated-sludge treatment plants (Stutz, 1966). Full-scale plant operation by Monsanto (Coley and Stutz, 1966; Stutz, 1966) has shown that parathion process wastes can be treated at the plant without dilution. Neutralization, pH control, and nutrient addition precede activated sludge treatment. Seven to ten days aeration was employed, with 100 to 150% sludge return. Suspended solids levels were maintained at 15,000 - 18,000 mg/l (30% volatile). The COD was reduced from 3,000 to 100 mg/l and suspended solids in the effluent were 60 mg/l. BOD reduction was near 90% and the phenol content was near 0.1 mg/l. Parathion degradation was not reported. The clarified effluent plus waste solids were sent by sanitary sewer to a conventional municipal plant for final treatment.

2) A study on 2,4-D wastewater shows that it can be successfully treated by the activated-sludge process provided that dilution and nutrient requirements

are satisfied (dilution factor of 3.40 was used for industrial effluent containing up to 3,000 ppm of 2,4-D; the nutrient requirements were satisfied by mixing settled sewage with industrial effluent in a ratio of 1:600) (Mills, 1959). Treatability studies of 2,4-D and 2,4,5-T acid wastes (Ford and Gloyna, 1967) indicate that wash wastewaters had to be diluted twenty to one with tap water before biological treatment could be used (Figure 18). The waste concentration had to be less than 1,800 mg/l (as COD) for effective treatment (Figure 19). Significant COD and BOD removal were accomplished if proper seed and sufficient dilution were provided. Recently, a detailed full-scale study indicated that 2,4-D and 2,4,5-T wastes can be treated in an aerated lagoon system when diluted at least thirty to one with municipal sewage. After three days in the aeration basin and several weeks detention in a stabilization pond, 87 to 94% removal of chlorophenols and 49 to 80% removal of chlorophenoxy acids were achieved (EPA Report 12130 EGK 06/71).

3) A malathion degradation study by Randall (1963) showed that the activated sludge process is highly effective in removing malathion from solution. It also showed that daily applications of malathion to an activated sludge system do not result in an increasing buildup of malathion residue.

4) A study made on microbial degradation of DDT, PCNB (pentachloronitrobenzene), and dieldrin showed that actinomycetes, filamentous fungi, and streptomyces degrade PCNB and that several actinomycetes dechlorinate DDT to DDD but no microorganisms tested degraded dieldrin (Chacko, et al., 1966). However, another study shows that a few soil microbes (unspecified) are very active in degrading dieldrin to various metabolites (Matsumara, et al., 1967).

5) A study made on microbial degradation of 2,4-D 2-CPA, 4-CPA, and MCPA showed that bacterial

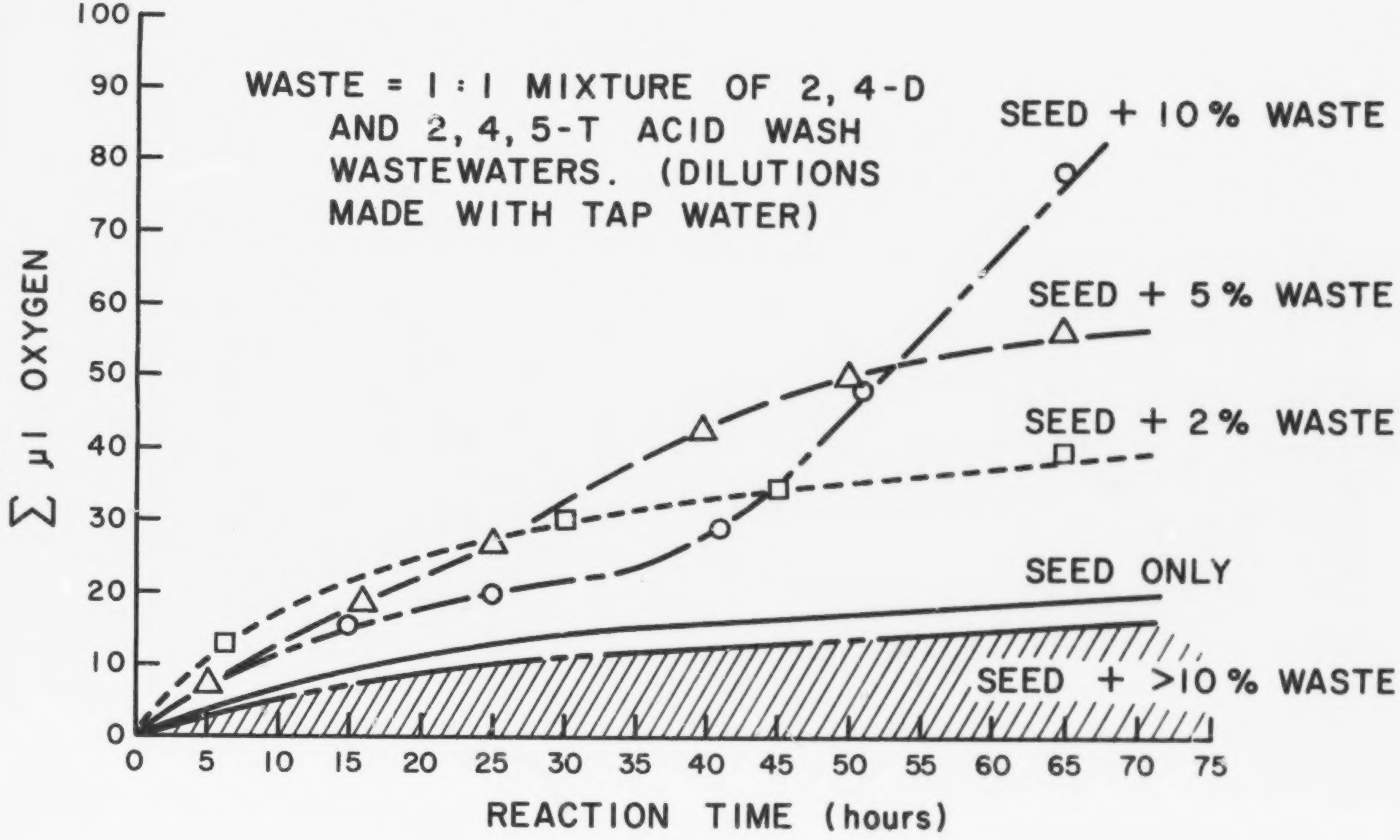


Figure 18. Dilution Effect on Respiration Rates.

Source: Ford and Gloyna, 1967.

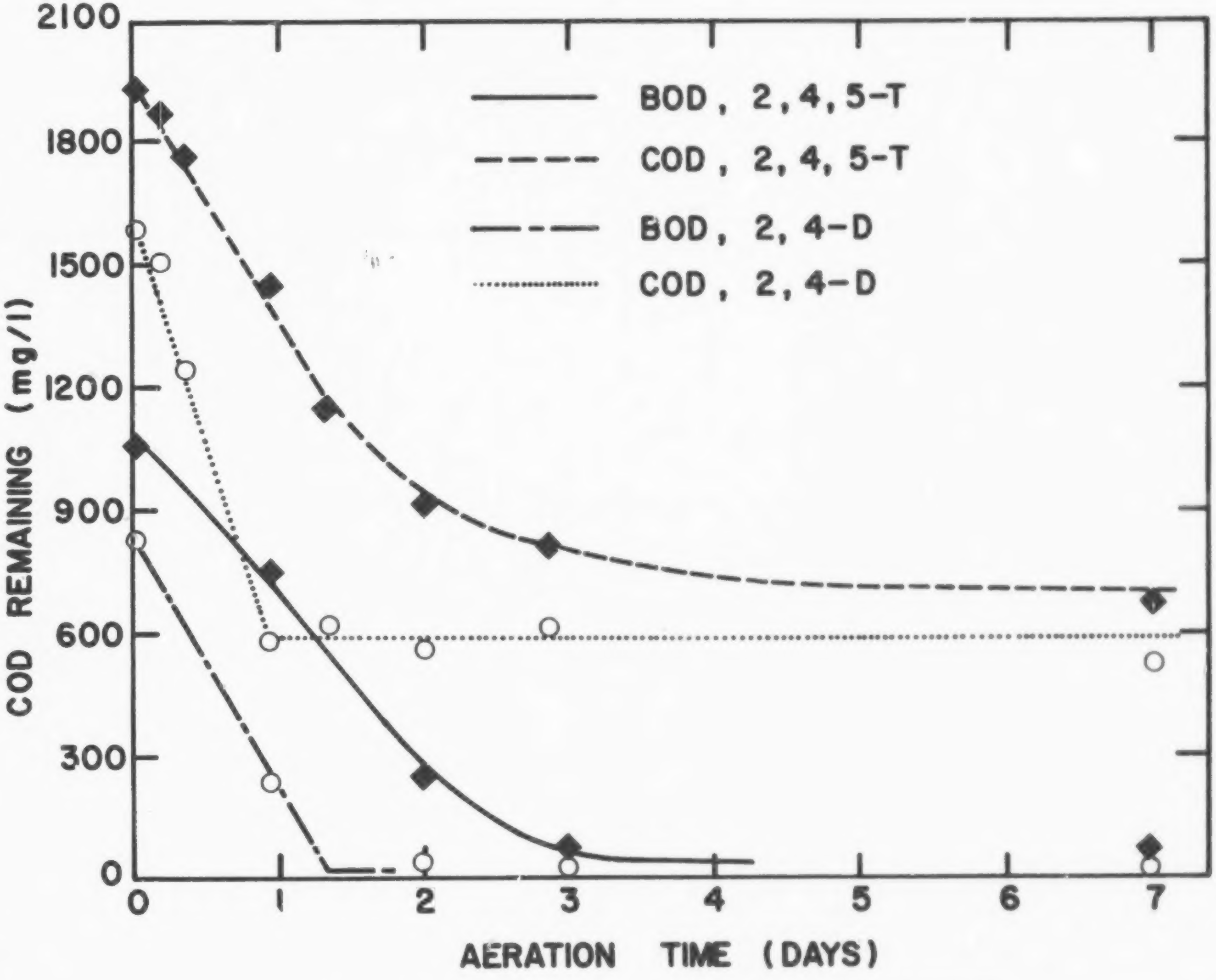


Figure 19. Batch Aeration of 2,4-D and 2,4,5-T Acid Wastes.

Source: Ford and Gioyna, 1967.

enzymes catalyze the degradation of these pesticides (Loos, *et al.*, 1967). Extracts from organisms cultured in media containing phenoxyacetate herbicides converted these compounds rapidly to phenols when added to solutions containing the herbicides.

6) A study of Bounds and Colmer (1965) made on detoxification of herbicide by streptomyces gives positive results for 2,4-D, silvex, fenac, and dalapon. It also gives negative results for CDAA, CIPC, and 2,4,5-T.

7) A study made on the degradation of γ- BHC (lindane) in simulated aerobic and anaerobic lake impoundments shows that anaerobic degradation is considerably more rapid than aerobic degradation. It also shows that degradation leads to detoxification (Newland, *et al.*, 1968).

8) On the degradation of selected chlorinated hydrocarbon pesticides, Hill and McCarty (1967) showed that many of these pesticides are degraded under suitable biologically active, anaerobic conditions. It also showed that anaerobic degradation is faster than aerobic degradation for most of the chlorinated hydrocarbon pesticides studied (exceptions were heptachlor epoxide and dieldrin which were very persistent in both environments). It indicates that extractable degradation products are more common under anaerobic than under corresponding aerobic conditions. It ranks the pesticides studied and their extractable degradation products in the following approximate order of increasing persistence under anaerobic conditions: lindane, heptachlor, endrin, DDT, DDD, aldrin, heptachlor epoxide, and dieldrin. Figures 20-25 show the anaerobic degradation rates for the pesticides studied under a variety of conditions.

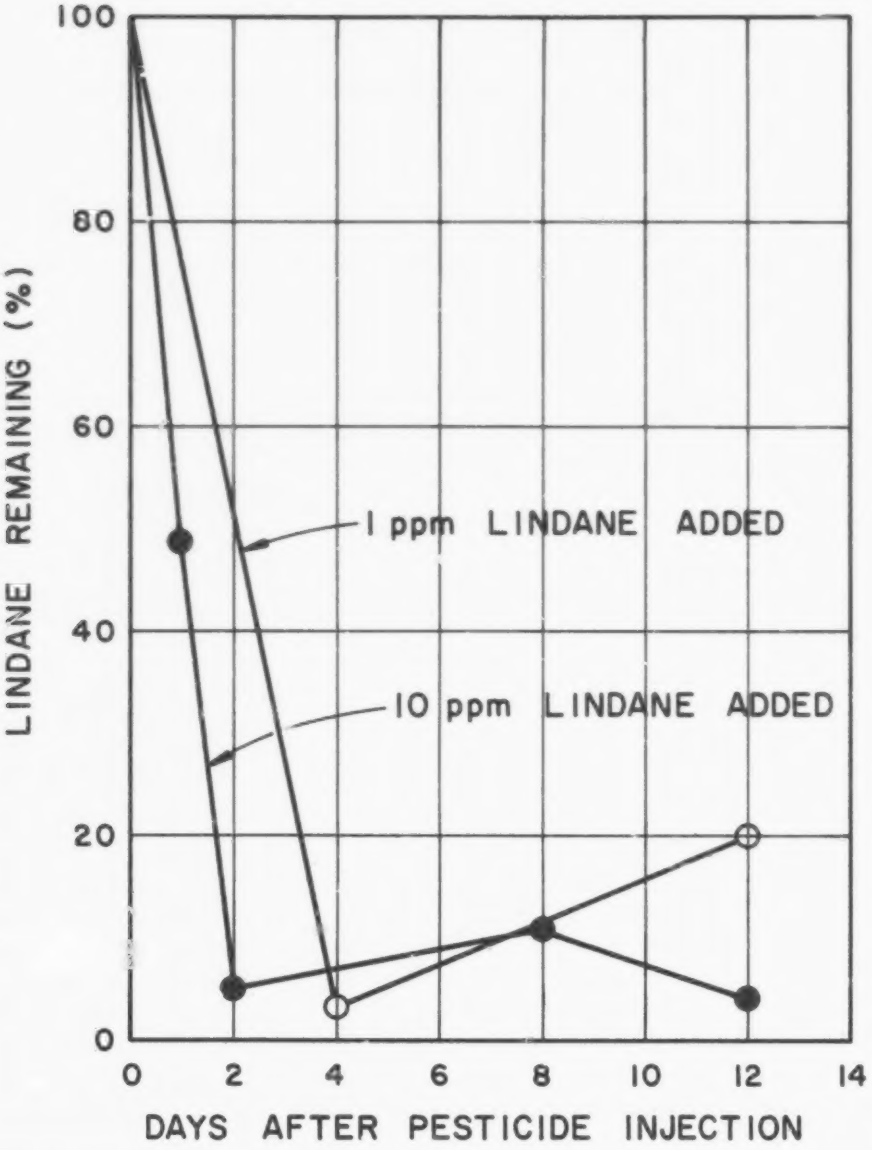


Figure 20. Anaerobic Degradation of Lindane in Sludge containing 1.5% dry solids (56% volatile). The pesticides were dissolved in acetone injected into one-gallon reactors and the systems were agitated on shakers.

Source: Hill and McCarty, 1969.

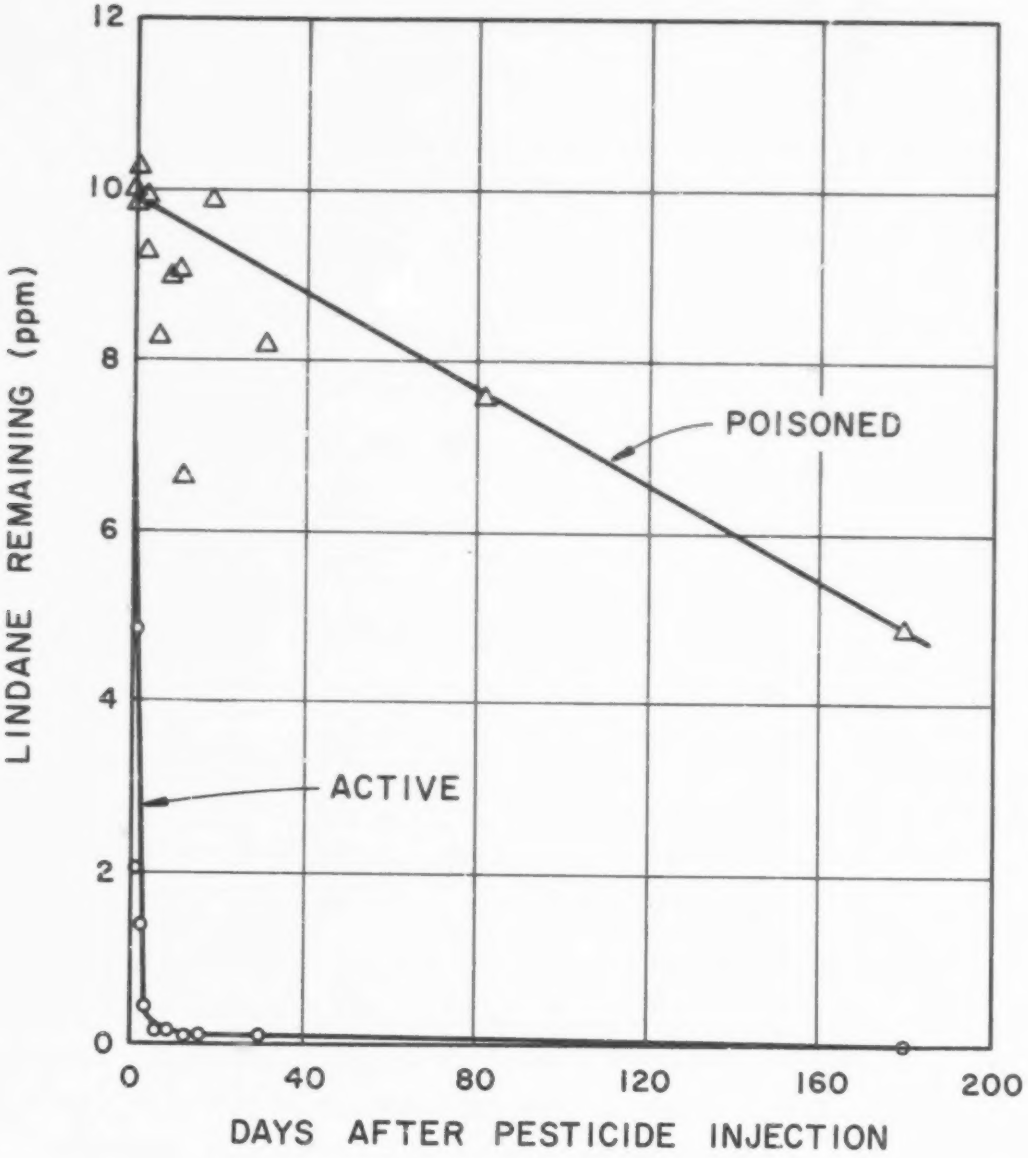


Figure 21. Anaerobic Degradation of Lindane in Active and Poisoned (4 g/l cobaltous and mercury salts) Sludge at 35° C. 10 ppm Lindane Added Initially.

Source: Hill and McCarty, 1967.

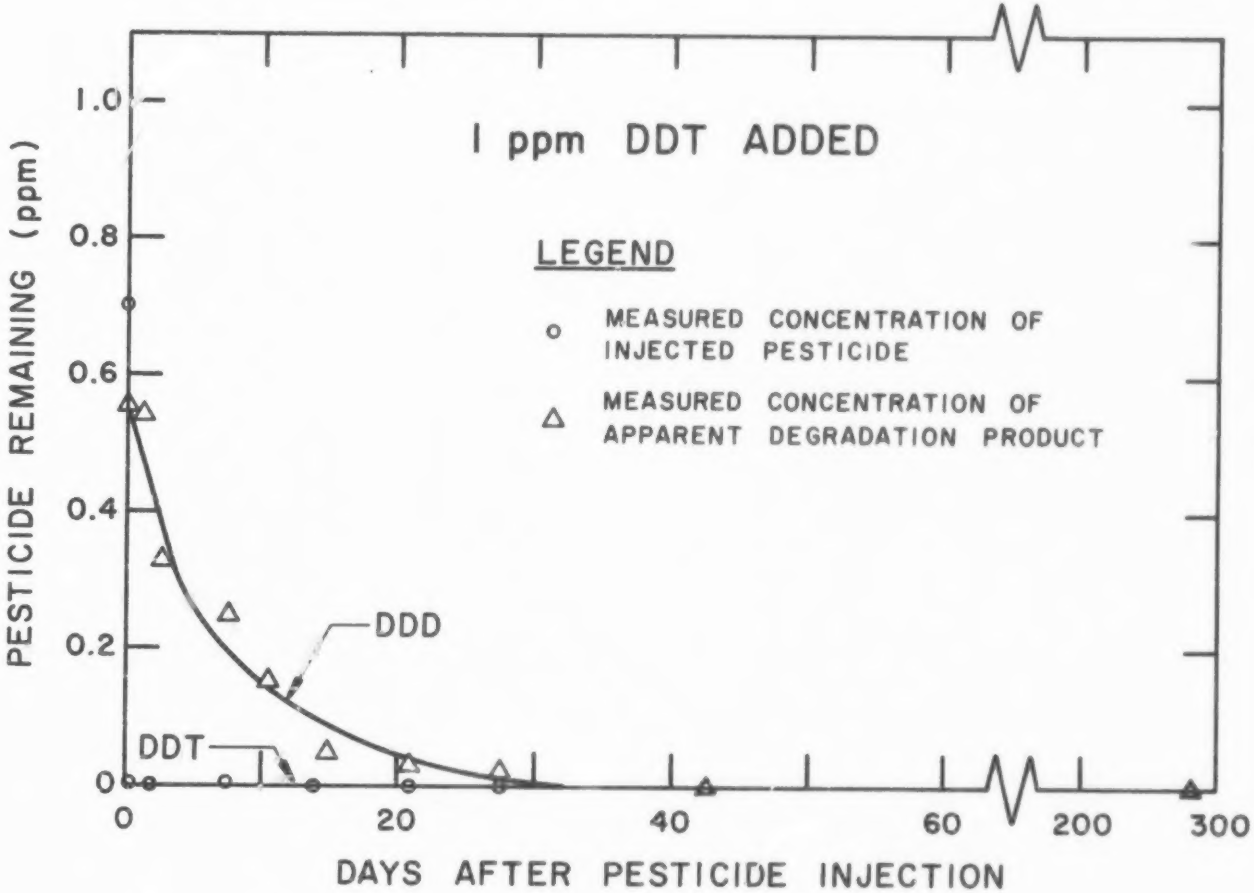


Figure 22. Anaerobic Degradation of Single Pesticides in 3500 ml of 7.2% total solids (48% volatile) sludge at 35°C. Similar studies on heptachlor and aldrin were reported by the authors.

Legend: o Measured Concentration of Injected Pesticide
△ Measured Concentration of Apparent Degradation Product

Source: Hill and McCarty, 1967.

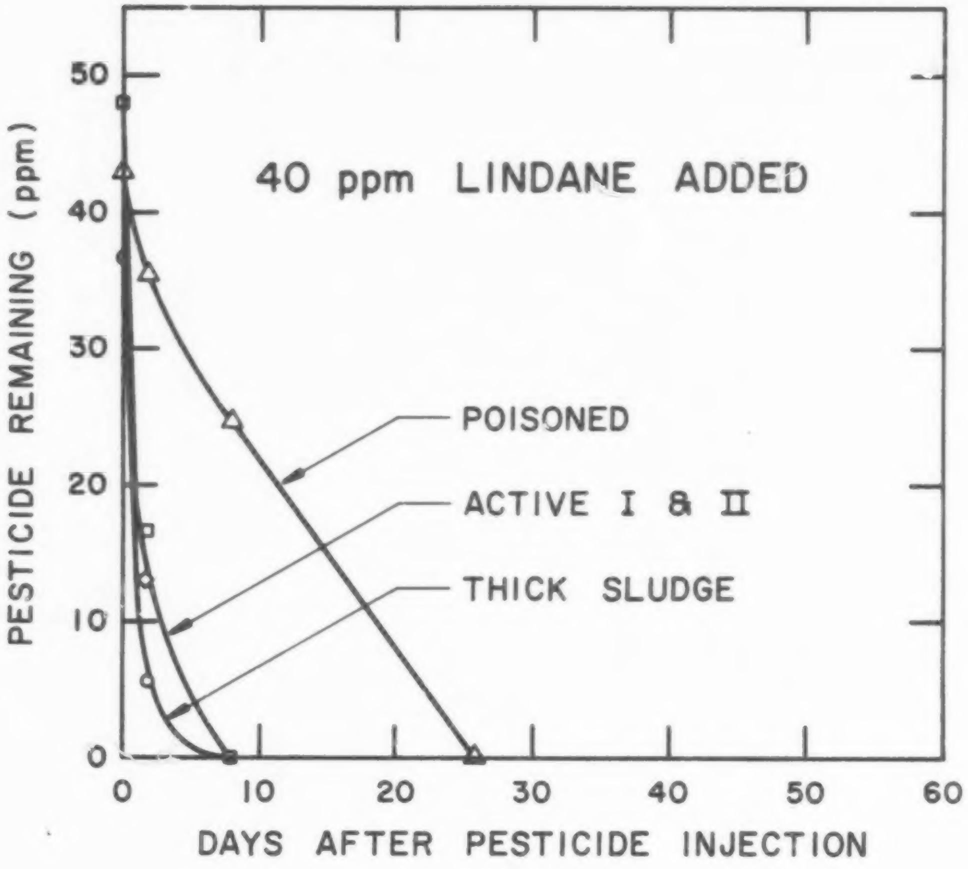


Figure 23. Anaerobic Degradation of Pesticide Mixtures in Thick Sludge at 35°C (pesticides without extractable degradation products). Poisoned with 0.5 g/l mercurous chloride as mercury. One-gallon sludge units containing 7.2% solids (thick sludge) or 4% solids (Active I,II, and Poisoned) were used. Similar studies on aldrin, heptachlor, epoxide, and dieldrin were reported by the authors.

Source: Hill and McCarty, 1967.

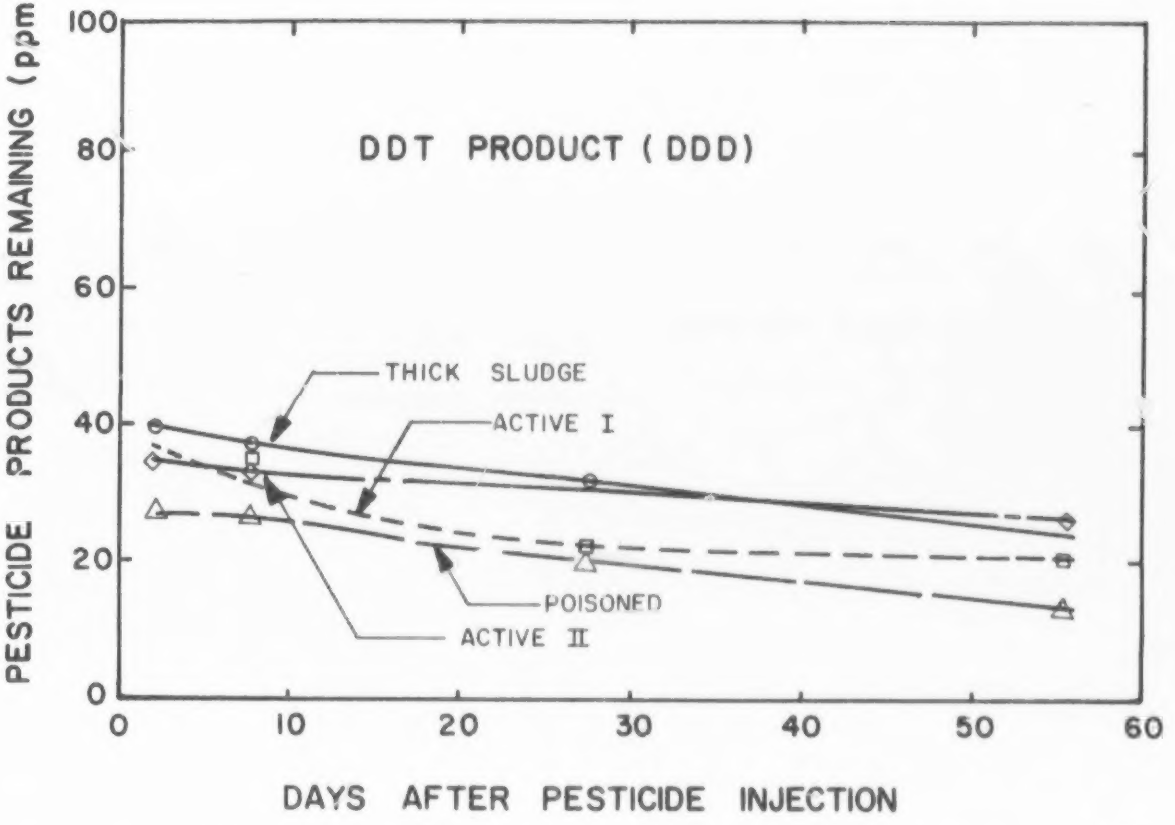


Figure 24. Anaerobic Degradation of Pesticide Mixtures in Thick Sludge at 35°C (pesticides with extractable degradation products). Poisoned with 0.5 g/l mercurous chloride as mercury. One-gallon sludge units contain 7.2% solids (thick) or 4% solids (Active I and II and Poisoned) were used. Similar studies on heptachlor, heptachlor products, endrin, and endrin products were reported.

Source: Hill and McCarty, 1967.

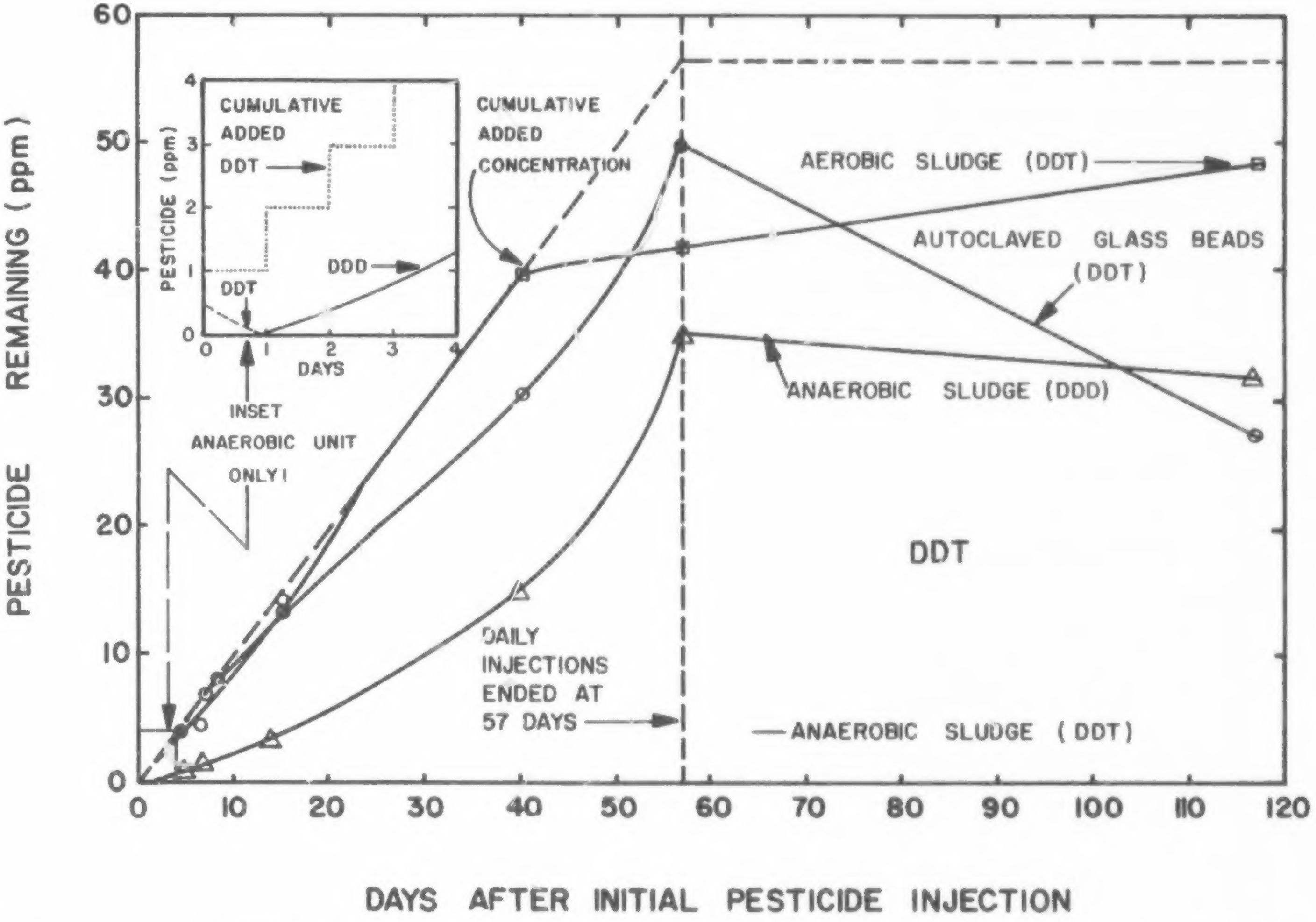


Figure 25. Pesticide Degradation in Dilute Sludge at 20°C (daily injection units). Quantity injected to give incremental increase of 1 ppm. Five-gallon sludge units were used. The sludge was digested wastewater sludge diluted 19:1 with tap water. Similar studies on heptachlor, epoxide, aldrin, and lindane were reported.

Source: Hill and McCarty, 1967.

9) An aerobic study made on malathion shows that the reduction of malathion concentration in water is greatly increased by increasing the rate of aeration. It also shows that activated sludge may be acclimated to daily feedings of malathion at a level of 100 mg/l (Randall, 1963).

Foam Fractionation

A foam fractionation study by Whitehouse (1967), was conducted on aldrin and dieldrin. The following is a list of the surface active agents used and the results of the study.

Surface active agents:
- cationic (Aerosol C-61)
- anionic (alkyl benzene sulfonate)
- nonionic (Dowfax 9N9)

Results: This study showed that the cationic surface agent, Aerosol C-61, removes aldrin and dieldrin more effectively than the anionic and the nonionic surface active agents tested. It also showed that repeated dosing is more effective than a single dose of the same total quantity. Table 15 shows the cumulative pesticide removed with three repeated doses of 10 mg/l of Dowfax 9N9, 10 mg/l of ABS (Alkyl benzene sulfonate), and 2.5 mg/l of Aerosol C-61. Pesticide solution samples of 500 ml were used.

Disposal Methods

Most disposal methods used for pesticidal wastes are closely related to the wastewater treatment methods previously discussed. However, there are some disposal methods which may not directly involve treatment; these include combustion, burial, disposal at sea, and deep-well injection. Such methods may be used solely as alternatives to treatment or they can be utilized in conjunction with treatment processes. A brief discussion of these methods follows:

Combustion

Incineration is a popular disposal method for concentrated waste streams. Most organic compounds (liquid and gaseous) can be effectively destroyed by the method, but other components of the waste streams often

Table 15. Cumulative Pesticide Removed - Foam Foundation

	Cumulative Aldrin			Cumulative Dieldrin		
Dose No. (Equal dose per treatment) Surface Active Agents (dose size)	1	2	3	1	2	3
10 mg/l of Dowfax 9N9	37%	57%	64%	40%	75%	86%
10 mg/l of ABS	53%	65%	71%	52%	77%	89%
2.5 mg/l of Aerosol C-61	65%	80%	83%	83%	95%	97%

Each Sample = 500 ml
Aldrin Dose = 0.02 mg/l
Dieldrin Dose = 0.035 mg/l

Source: Whitehouse, 1967.

cause significant problems. Nitrogen compounds present in combustion air and in many pesticide manufacturing wastes invariably produce oxides of nitrogen (NO, NO_2, etc.) when burned. Since these gases are of importance in the atmospheric reactions which produce photochemical smog, regulations against their production are often severe and will no doubt become more restrictive in the future. Sulfur-bearing compounds may produce significant quantities of sulfur dioxide and sulfuric acid as reported by Tabor (1970). Regulations restricting SO_2 emissions are already in effect in almost all states.

Compounds containing heavy metals including lead, mercury, and arsenic should be burned only if proper precautions are taken to control atmospheric emissions. Lead and mercury salts as well as arsenic can escape the combustion chamber and travel great distances, contaminating large areas. Low levels of these compounds may produce recognizable effects in plants or animals as well as people. Compounds containing chlorine produce hydrochloric acid, which can cause serious corrosion problems in the incinerator and in some cases significant downwind pollution problems.

These problems make it difficult but not impossible to burn many pesticide wastes. Temperature control, excess air control, fuel and waste feeding techniques, and proper incinerator design can all reduce the magnitude of the emission problems. A well-designed and operated air cleaning device (which will normally constitute a major capital investment) can remove many of the gaseous pollutants and eliminate virtually all of the particulates. These devices should be included in the original design of the incineration equipment and not merely added at a later date when air pollution problems become obvious.

Table 16 summarizes results of a combustion study made by Kennedy, et al. (1969) on nineteen pesticide formulations at five different temperatures. Most pesticides showed a high percent loss on combustion. However, the data shown indicate that care must be taken to provide adequate combustion temperatures and contact times for complete disposal. The tests were made in controlled temperature chambers where adequate oxygen was available. Commercial formulations of the pesticides were burned rather than waste streams. The data indicate that most pesticide compounds are destroyed effectively by burning at 800°C to 1000°C. Exceptions are atrazine, zineb, bromocil, dalapon, DSMA, and sevin.

Table 16. Percent Loss on Combustion of Commercial Formulations of Pesticides at Five Temperatures

Commercial Formulation	Loss (%) at				
	600°C	700°C	800°C	900°C	1000°C
Picloram	90.8	91.8	95.6	98.7	99.2
Atrazine	87.8	88.1	88.8	88.9	89.0
Nemagon	99.6	99.6	99.6	99.6	99.6
Trifluralin	99.7	99.8	99.8	99.8	99.8
Malathion	95.3	96.0	96.3	96.4	96.7
2,4,5-T	99.9	99.9	99.9	99.9	99.9
Zineb	70.1	71.3	71.5	72.7	72.8
Vernam	99.6	99.6	99.6	99.6	99.6
Paraquat	98.3	98.6	99.0	100.0	100.0
Dicamba	98.6	98.7	98.9	99.0	99.4
Bromacil	88.8	89.1	89.4	90.5	91.3
Dieldrin	99.1	99.4	99.5	99.5	99.5
DDT	99.2	99.3	99.7	99.9	100.0
Dalapon	64.3	64.3	67.8	73.8	91.0
2,4-D	99.8	99.9	99.9	99.9	99.9
Diuron	94.6	95.0	95.4	95.5	95.7
DNBP	99.8	99.8	99.8	99.8	99.8
DSMA	80.6	80.7	80.7	81.2	81.2
Sevin	88.7	88.8	88.8	89.1	89.5

Source: Kennedy, _et al._, 1969.

In a combustion chamber, the toxic compounds may undergo decomposition by oxidation, pyrolysis, isomerization or polymerization. If the combustion temperature is too low, the residence time in the chamber is too short, adequate air is not present, or the waste is not well dispersed to expose a large amount of surface area, then complete destruction of the toxic compounds may not occur. In the case of organophosphate insecticides, toxic isomers of the original compound may be produced (Smith and Ledbetter, 1970).

Many of the major problems associated with incineration of pesticide wastes in the past resulted from failure to consider the constituents of the waste other than toxic materials. Pilot studies should always be conducted to provide information on effluent gas and particulates from the incinerator exhaust. In a well-designed, well-operated incinerator, phosphorus-containing compounds produce P_2O_5 and phosphoric acid, which can result in a heavily-persistent white plume visible for long periods of time. High potassium or sodium levels in a waste can produce hygroscopic salt nuclei that cause visibility problems in humid atmospheres (Marks, 1965). In addition, the salt particles may be air pollutants of consequence, especially in agricultural areas.

Burial

Burial of pesticide wastes is a common practice. Solid, semi-solid and liquid wastes are often buried in landfill or placed in open pits. The liquid and semi-solid wastes are usually sealed in containers for transport to land fill sites or placed in the open pit areas in bulk. Therefore, the two methods differ considerably and will be discussed separately.

The land fill type disposal method normally involves opening a trench, often fifteen feet or more in width and up to twelve feet deep, depositing the waste material in the trench, compacting the material (thus rupturing any containers present) and covering the waste daily with a minimum of six inches of compacted earth. The final fill cover should be at least 18 inches deep in order to isolate the waste material. Where topography permits, the waste material can be used to fill low areas without opening a trench. Borrow pits are necessary to provide the necessary cover material. However, if this procedure is used, special measures must be taken to provide for surface drainage around the fill site.

Subsurface pesticide movement is possible and should be considered especially in highly permeable soils. In tight, clay meterial and high organic content soils, most pesticides will move slowly as rainwater and landfill leachate pass through the soil. Studies indicate that chlorinated hydrocarbons including dieldrin (Eye, 1968) and aldrin migrate only a few feet in natural soils over periods of years. The U.S.G.S. (Rima, et al., 1967) reports little horizontal movement of dieldrin, endrin, heptachlor and heptachlor epoxide from a landfill located at a site underlain by a nearly horizontal strata composed of deposits of sand, silt and clay. However, it was reported that the subsurface disposal had produced a zone of contamination directly beneath and peripheral to the landfill. Laterally the limits of the zone of contamination appeared to be confined to 25 feet or less from the trench margins. The depth of the zone, however, extended nearly to the water table, 90 feet beneath the land surface. In addition, surface waters in a nearby stream contained traces of the four pesticides, probably from surface runoff.

Organophosphate pesticides also move slowly in soils, as shown by King and McCarty (1966). In a gravelly sand soil (5% clay) six to eight feet of eluted water was required to move 25% of the applied thiamate through one and one-half inches of soil. In a heavy clay soil (37% clay), after 28 feet of elute water, only 5% of the same pesticide had moved through the soil.

These studies indicate that, if proper care is taken, landfill area can be a suitable disposal method. The soil type should be such that waste migration is minimized (i.e., high clay or high organic content). The water table should not be near the disposal site (a minimum of 10 feet between trench bottoms and the water table should be maintained). Surface flow should be controlled to prevent erosion and surface water contamination. Site management should be strict enough to prevent spills, leaks and improper dumping or covering. A monitoring program should be instituted which would include surface water sampling, ground water sampling below the fill, and water sampling at any nearby drinking water sources. Table 17 shows in generalized fashion the relative mobility of various pesticides in "typical" soil.

It should be realized that a natural soil system is never a simple homogenous medium that can be modeled with assurance. Undetected layering, faults and fractures, and drainage channels to ground water can cause unforeseen problems. Since the rate of travel of chemicals in a soil-water system is dependent on the solubility and sorption characteristics of the pollutant and the physical characteristics of the aquifer, detailed study and sampling should be conducted before a fill site is chosen.

Table 17. Relative Mobility of Pesticides in Soils*

Immobile	Slightly Mobile	Mobile
Aldrin	Atrazine	2,4-D
Chlordane	Simazine	2,4,5-T
DDT	Prometryne	MCPA
Dieldrin	Azinophosmethyl	Picloram
Endrin	Carbophenthion	Fenac
Heptachlor	Diazinon	
Toxaphene	Ethion	
TDE	Methyl Parathion	
Lindane	Lindane	
Heptachlor Epoxide	Heptachlor Epoxide	
Trifluralin	Parathion	
	Phorate	
	Diuron	
	Monuron	
	Linuron	
	CIPC	
	IPC	
	ERTC	
	Pebulate	

*Mobilities are based on soil thin-layer chromatography - mobile compounds move between R_f 1.0-.65, slightly movile .64-.10, and immobile .09-.00. (R_f = "relative to fructose").

Source: Working Group on Pesticides, 1970.

Pesticides buried in a landfill may be degraded biologically or chemically. Unsaturated, branched chain compounds of high molecular weight are less susceptible to degradation than the saturated short chain compounds. Aromatics are also resistant to degradation in soils. The principal factors that govern the stability of pesticides and related halogenated and phosphorylated compounds include soil texture, humus content, temperature, moisture and pH. The half life of these materials may vary from a few weeks to several years (Witt, 1971). A listing of a number of representative pesticides and their persistence in "typical" soil is given in Appendix A.

The open dump, or open pit disposal method, is also used by many pesticide manufacturers. The pit disposal method consists of placing wastes in an open pit or trench without compaction or cover. The wastes are exposed to the elements until the pit is filled. When full, the pit is covered with earth and abandoned. These methods are used because of their relative cost. Landfill operation requires labor and equipment costs of at least $1.00 per ton of waste plus the cost of haul. Pit disposal can be accomplished for almost no cost if the pit is located on or near the plant site.

Pit disposal can produce the same types of contamination as a landfill. Since abandoned sand and gravel pits, rock quarries and other naturally occurring topographic features are often utilized as disposal pits for reasons of availability and economy, the probability of large scale subsurface contamination is increased. In general, the problems, both real and aesthetic, associated with pit disposal make it undesirable. Odors, volatile toxic gas releases, and increased likelihood of water contamination are potential problems. In addition, the probability of accidents near the pit is high, since haphazard dumping is usually employed. Even after final cover, the disposal site is subject to significant settlement, cracking, and perhaps surcharge during heavy rains. For these reasons, the Working Group on Pesticides recommends that "this method of pesticide waste disposal should be discouraged except under extremely favorably geologic conditions and where the site is very remote from producing wells" (Working Group on Pesticides, 1970).

Burial practices are receiving close scrutiny by various regulatory agencies. The degree of control and severity of the regulations will continue to increase and care must be taken when choosing the method as a long term disposal practice. A regulation to control waste burial proposed by the State of California is included in this report as Appendix C since it is typical of regulations which may be expected in the future.

Ocean Dumping

A disposal method currently used for some manufacturing wastes generated at locations near oceans or the Gulf of Mexico is ocean dumping. This practice is now receiving much attention and will probably be subject to highly restrictive legislation in the near future. Presently, concentrated liquid and semi-solid wastes are carried by barge in bulk form or in containers to dumping sites several miles to several hundreds of miles offshore. There the wastes are discharged overboard in the wake of the barge. Containers are weighted to insure that they sink or are pierced after dumping. In 1968, approximately 330,000 tons of pesticide wastes were dumped in this manner (Anon., Chem. and Engr. News, 1970). Dumping costs average slightly less than $4.00 per ton (Witt, 1971).

Presently, regulatory activity and authority is confusing and inadequate. "States do not exercise control over ocean dumping and generally their authority to regulate ocean dumping is also largely confined to the territorial sea. The Coast Guard enforces several federal laws regarding pollution, but has no direct authority to regulate ocean dumping. The authority of the Federal Water Quality Administration (now WQO of the EPA) does not provide for issuance of permits to control ocean dumping" (Council on Environmental Quality, 1970). However, this practice is changing. The State of New Jersey is considering ocean dumping regulations which can apply to pesticidal wastes. (Appendix D contains a statement by Governor Cahill of New Jersey on this subject). Indications are that regulations restricting ocean dumping will also be forthcoming from the Congress. These regulations will require that strict criteria be followed in selecting dumping sites and performing dumping operations.

If ocean dumping continues to be utilized for waste disposal, certain factors must be carefully considered to insure minimum environmental degradation. Site selection is important, and consideration of tidal action, water depth, currents, proximity to shore, island or fishing grounds, bottom characteristics, etc., must be included. In addition, detailed assessment of the possibility of the following factors should be conducted.

1. Surface Slicks
2. Depletion of Dissolved Oxygen
3. Acute Toxicity
4. Long-Term Toxicity Effects

Estimates of dilution can be based on models such as one developed by Pearson (1968) and Ketchum and Ford (1952) and modified by Smith (1969):

$$\frac{C}{Co} = \left\lceil 98d\,(KV^2t)^{1/2} \right\rceil / Q^{1/100}$$

where:

$\frac{C}{Co}$ = average dilution along the axis of the waste plume at time, t, after passage of the barge
d = assumed mixing depth (ft)
K = eddy diffusivity (ft^2/sec)
t = time elapsed after passage of the barge (sec)
V = barge velocity, relative to plume (ft/sec)
Q = waste discharge rate (gallons per hour)
K = $0.001\ L^{4/3}$
L = depth of the water at the dumping site

Using these equations and assuming a water depth (and mixing depth) of 300 feet, barge velocity of 5 knots and a discharge rate of 120,000 gallons per hour, the estimated dilution along the plume center line would be:

Distance behind barge (ft)	Time after passage (min)	Dilution factor
100	0.19	30,000
1,000	1.95	94,000
10,000	19.50	300,000

Recent studies (Smith, 1969) indicate that at least in one case, the above equations overestimate the dilution factor by a factor of four or five. Even so, this brief analysis indicates that rapid dilution of both BOD and toxic components occurs in the barge wake. However, studies of the effects of low-level concentrations of waste materials should be conducted before indiscriminant dumping occurs.

In addition, special detail should be given to wastes sealed in drums. These drums may be weighted and allowed to sink or they may be pierced after dumping. In either case, these drums will release wastes below the surface in relatively still waters where mixing is limited. Severe local problems may result from the contents of these containers.

Deep Well Disposal

Subsurface, and particularly deep subsurface, disposal of waste is receiving increased attention from industry and regulatory agencies alike as plant production increases with its proportionate increase in waste effluent. In order to prevent the cost of waste disposal from reaching astronomical proportions, subsurface disposal has been utilized by several plants having large quantities of concentrated water-borne wastes.

It is estimated that about 240 municipal and industrial deep wells have been installed in the U.S. since 1950 (Anon., Industrial Waste, 1971). However, increased concern over the fate of the injected wastes has lead to some questions concerning the safety of this practice, and future regulations controlling deep well disposal promise to be restrictive. The U.S. Geological Survey has been of assistance in determining the geologic structure of the areas considered for subsurface disposal. The wells must be located over deep permeable rock formations which have suitable hydrologic properties to receive and contain the volume of waste injected. Extreme care must be exercised in the construction of the well to prevent any possible contamination of the fresh water zones. The required depth of the well is dependent upon a number of factors including the slope of the aquifer being considered for injection, the salinity and/or purity of the water in the aquifer, ease or difficulty in drilling, and the ability of the formation to accept the additional liquid material.

The detailed geological data for the area should be collected to locate and define the extent of the disposal formation and to trace the pollutional movement. Extensive studies should be conducted to test the wastewater and formation water compatibility. The State of Texas requires a detailed record of the subsurface geologic data covering a 2-1/2 mile radius around a proposed disposal well before a permit will be issued. In addition, all unplugged wells in the vicinity of the disposal well must be logged. The Injection Well Act of the State of Texas is included in this report as Appendix B.

The well itself should be constructed by capable drilling contractors in accordance with the requirements of the governing regulatory agencies. The well should be designed to protect all fresh water formations and other formations which may yield future natural resources. It should be constructed of corrosion-resistant materials of reliable quality. Disposal well failures have been associated with inadequate construction or poor materials more often than with improper operation or incompatibility of the waste fluid with the formation. Figure 26 shows a diagram of a completed liquid waste injection well (Anon., National Agricultural Chems. Assn., 1965 and Warner, 1965).

Since deep well disposal places the waste in a remote location where its ultimate fate cannot be adequately determined, the practice of subsurface injection is receiving critical review in many agencies. The uncertainties associated with this type of disposal can make it questionable, especially for long-lived pesticides and pesticidal wastes.

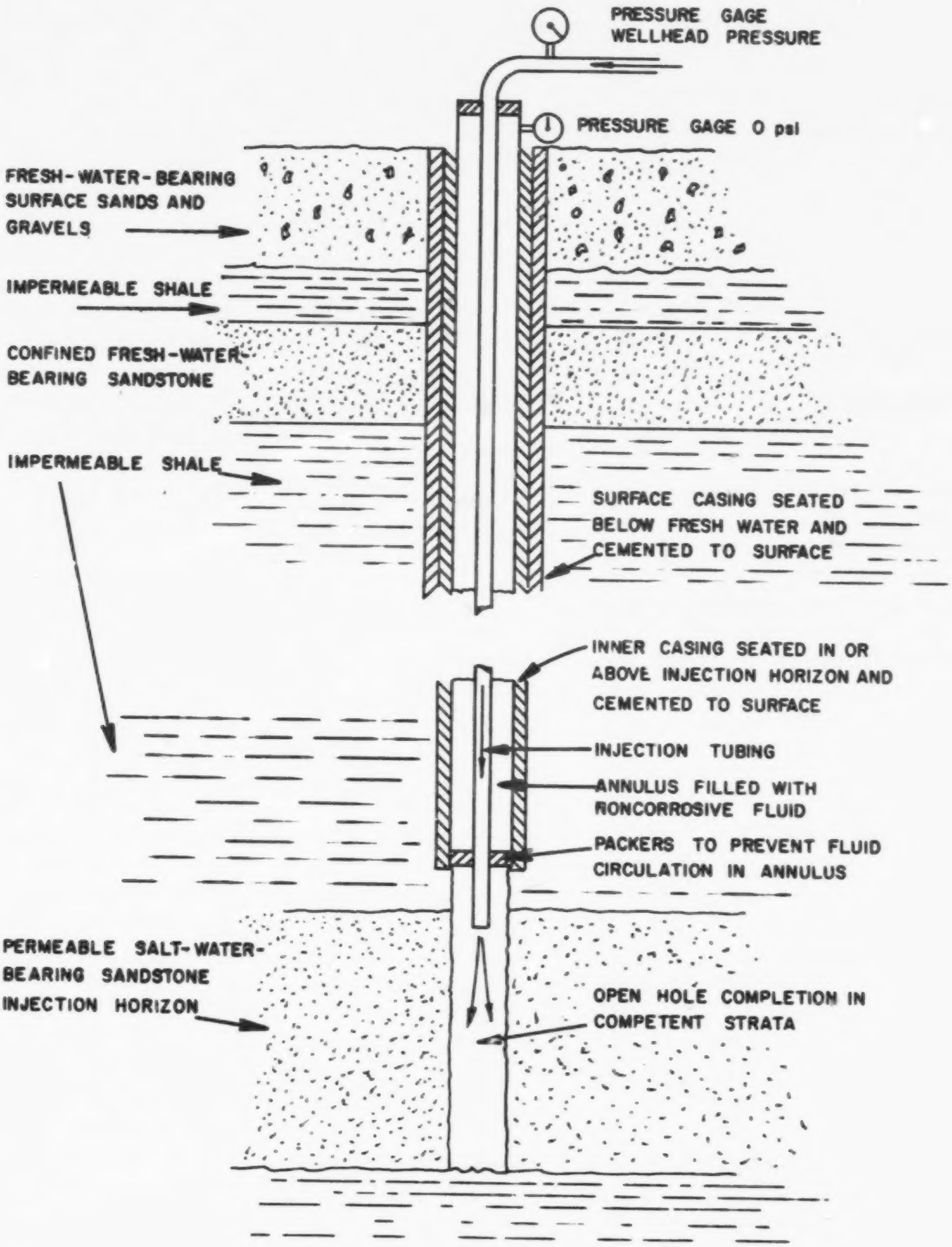

PRESSURE GAGE
WELLHEAD PRESSURE
PRESSURE GAGE 0 psi
FRESH-WATER-BEARING SURFACE SANDS AND GRAVELS
IMPERMEABLE SHALE
CONFINED FRESH-WATER-BEARING SANDSTONE
IMPERMEABLE SHALE
SURFACE CASING SEATED BELOW FRESH WATER AND CEMENTED TO SURFACE
INNER CASING SEATED IN OR ABOVE INJECTION HORIZON AND CEMENTED TO SURFACE
INJECTION TUBING
ANNULUS FILLED WITH RONCORROSIVE FLUID
PACKERS TO PREVENT FLUID CIRCULATION IN ANNULUS
PERMEABLE SALT-WATER-BEARING SANDSTONE INJECTION HORIZON
OPEN HOLE COMPLETION IN COMPETENT STRATA

Figure 26. Schematic Diagram of a Waste Injection Well Completed in Competent Sandstone.

Source: Warner, 1965.

CHAPTER VI

TREATMENT & DISPOSAL PRACTICES PRESENTLY EMPLOYED

A number of major pesticide manufacturing plants and several formulating operations were visited and their treatment facilities were observed. The information presented in the following discussion is based on the results of these site visits. It is impossible to present detailed design and operational data applicable to all types of pesticidal wastes. In many cases such information is not known and in other cases the data cannot be released for manufacturing process security reasons. Therefore, the information presented of necessity will be general in nature, but should be useful as a basis for preliminary decision-making and initial design requirements for waste treatment facilities.

In-Plant Control

One of the most obvious methods of minimizing pollution from pesticide manufacture is to institute control techniques that will reduce the loss of raw material, solvent and product. Good housekeeping measures have proved beneficial in several pesticide manufacturing plants. Automatic monitoring and alarm equipment installed at various locations in the waste collection system of at least one major pesticide and petrochemical manufacturer has given the treatment system operators the capability to 1) detect toxic slugs and route them to holding basins, and 2) to determine which plant processes are responsible for excessive waste discharges. Thus process managers can be held responsible for spills and poor housekeeping practices. The monitoring system has been instrumental in reducing the waste load on the treatment plant and has prevented toxic slugs from reaching the biological treatment systems.

Process areas in pesticide manufacturing plants should be sealed, diked and drained to a collection system to prevent contamination from surface run-off. Sumps in the drain system can concentrate heavy materials and often reduce the organic and toxic load to the treatment system. A major chlorinated herbicide manufacturer presently uses a sump system and a portable sump pump (pulled by a tractor) which periodically collects the sump contents and transports it to the incinerator feed tank for burning.

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Several plants, especially those involved in formulating, wash their spills, both liquid and powder, into sewers for collection and treatment. However, one major formulator has instituted a vacuum system for dust collection in the dry formulation area. A cyclone is used to concentrate the collected dust which is ultimately buried in a landfill. The elimination of the waterborne waste has proved beneficial since this was a major source of pesticide contamination in the plant effluent. No problems of equipment malfunction or excessive airborne emissions were reported.

Attempts to conserve or reuse water in pesticide manufacture have proven cost effective for some manufacturing processes, especially where ultimate disposal by deep well injection, burial, or ocean dumping is employed. However, if biological treatment is utilized, water conservation and reuse may result in wastes too concentrated with organic material, dissolved inorganics or toxic compounds for treatment. In several plants, dilution of the waste stream is necessary before treatment can be accomplished. Therefore, water conservation schemes should be critically reviewed in light of the proposed waste treatment plans.

Neutralization and pH Adjustment

In almost all cases, pesticide manufacturing wastes require some pH adjustment before treatment or discharge. The process waste streams invariably contain highly acidic and/or alkaline components. The term neutralization implies the adjustment of the wastewater stream pH to values near 7 (neutral). This step is required for:

a) corrosion control
b) reaction control on many chemical treatment processes
c) protection of stream organisms if direct discharge is employed
d) protection of microorganisms in biological treatment systems.

The most widely used neutralization agent in the pesticide industry is lime. In some cases, acid waste streams are merely passed through a lined trench which contains piles of 2-1/2" limestone or dolomite. As the waste flows through and over the limestone, the acids are neutralized and the calcium ions go into solution. pH levels as high as 5.3 and 5.5 may be achieved in these types of trenches. The pH of the trench effluent is dependent on limestone purity, residence time, waste acidity, etc.

Following the trench treatment, automatic pH monitoring and slaked lime feeding can be used to raise the pH level to the desired value.

Most plants have some caustic streams which are often mixed with the strongly acid streams before treatment. However, several operators have found that substantial chemical savings can occur if the caustic wastes are metered into the waste water stream after the limestone trench treatment rather than combining the waste streams ahead of the trench. Thus the caustic waste can replace the expensive slaked lime and the associated feeding equipment as the final pH adjustment agent. Excess caustic wastes may be added prior to the limestone pit if caustic waste storage is a problem.

In some cases, where excessive total dissolved solids may cause problems (incineration, deep well, etc.) neutralization agents such as anhydrous ammonia are used. This chemical is expensive but produces a neutralized stream with a much lower potential for air pollution from incineration or solids precipitation in a deep well stratum. The ammonium ion is combustible producing gaseous nitrogen oxides which cause no direct visibility problems, whereas sodium, calcium, and potassium salts produce submicronic crystals when burned and form persistent plumes in humid atmospheres. However, proposed regulations concerning ambient NO_x levels indicate that NO_x emissions will be curtailed in the near future. This may require that ammonia not be used without proper air cleaning equipment on the incinerator.

Mixing in the neutralization basin may be critical. Care must be taken to insure adequate mixing and detention for the neutralization reactions to reach completion, to reduce the effect of shock loads on biological or chemical systems following neutralization and to prevent sludge build-up in the neutralization basins. The latter factor is of prime importance with parathion and some chlorinated hydrocarbon wastes, since calcium salts often precipitate when lime neutralization is used. Continuous vertical paddles were recommended by several plant operators who used small rectangular neutralization basins.

Chemical Treatment

A variety of chemical treatment processes have been used to detoxify pesticide manufacturing wastes. Limited laboratory data are currently available on reaction rates, chemical doses and efficiencies. Most existing neutralization systems have been overdesigned to insure effectiveness. Table 18 summarizes the information on current chemical treatment practices gained from interviews with plant engineers and operators.

Ozone in concentrations of 4,000 to 6,000 mg/l can oxidize chlorinated hydrocarbon wastes effectively if adequate contact time is available. A study by Ford and Eckenfelder (1968) of DHC wastes from a dehydrochlorination unit showed that ozone dosages in excess of 4,000 mg/l were required for COD removals of 80% or more. However, their data indicated that ozone absorption efficiency begins to decrease rapidly when the ozone concentration exceeds 4,000 mg/l. The data are summarized in Table 19 and Figure 27. The wastes from the dehydrochlorination unit are similar to the phenolic wastes that result from some chlorinated herbicide manufacture, and the effectiveness of ozone treatment of DHC waste should be similar to ozone treatment of herbicide wastes.

Potassium permanganate can effectively be used as an oxidizing agent for some pesticide compounds. Organophosphate wastes (up to 7% organic) undergo substantially complete breakdown of the toxic compounds if held at 180°F for 20 minutes in a strong potassium permanganate solution. This reaction is carried out in a sealed, glass-lined vessel. The system is capable of treating an average flow of 14 gpm on a batch basis.

Acidification with HCl to pH of 2 or less will deodorize organophosphate wastes. The mercaptans (odorous compounds containing sulfur) are effectively destroyed if the acidified wastes are held at 215°F for 30 minutes or more. However, little reduction in toxicity occurs. Aldrin, dieldrin and endrin are susceptible to rapid dehydrochlorination in solutions with a pH below 3; but are stable in alkaline solutions. Often acid addition is the only treatment method used to detoxify wastes containing these pesticides.

Highly alkaline conditions can detoxify certain pesticidal compounds. Caustic soda is often used for pH adjustment to bring about hydrolysis of some chlorinated hydrocarbon and organophosphate manufacturing wastes. For example, 20% caustic added in an amount equal to one part caustic solution to 30 parts waste from an organophosphate plant is sufficient to produce complete hydrolysis in 1.5 hours when held at 200°F. An enclosed glass-lined vessel is used as a reaction unit. It has been found in at least one plant that relatively rapid hydrolysis of organophosphate wastes occurs at a pH of 9 at slightly elevated temperatures. For example, it was reported that at a temperature of 38°C, the half-lives of the toxic phosphate compounds vary from 4 to 96 hours. DDT, toxaphene, and related compounds undergo hydrolysis in strongly alkaline solutions but are relatively stable in

Table 18. Chemical Treatment

Type of Product	Waste Flow	Pretreatment	Chemical Treatment	Effectiveness	Post - Treatment	Remarks
Chlorinated Herbicides	50 gpm	Limestone Trench	Slake Lime Slurry	pH raised from 5.2 to 7.2	Aerated Lagoon	No precipitation occurs
Chlorinated Herbicides		None	Low grade Ca (OH) and Incinerator Scrubber Water Flash Mixed	pH raised to 8	Sedimentation	Effluent toxic at 300:1 dilution
Chlorinated Insecticides		None	Lime Addition	pH raised to 6.5	Incineration	Some precipitation
Chlorinated Insecticides	75 gpm	None	Caustic Scrubber Water and Ammonium Hydroxide added as needed	pH raised to 9 for hydrolysis	"Total" Evaporation	Rapid hydrolysis occurs

Table 18. (Continued)

Type of Product	Waste Flow	Pretreatment	Chemical Treatment	Effectiveness	Post - Treatment	Remarks
Organo-P Insecticides	500 gpm	Limestone Trench	Process Waste, Caustic added as needed	pH raised from 5.2 to 7.5 or 8	Activated Sludge	Higher pH required for methyl parathion
Organo-P Insecticides	100 gpm	None	Lime Addition	pH raised from <1 to 4.2	None	Biological treatment possible but not satisfactory
Organo-P Insecticides	40 gpm	None	20% caustic solution, 200° F for 1.5 hours;	Hydrolysis	"Total" Evaporation	Treatment in sealed reactors
			strong HCl 215°F for 5 hours;	Odor Control		
			potassium permanganate, 180° F for 20 minutes	Organic Oxidation		

Table 18. (Continued)

Type of Product	Waste Flow	Pretreatment	Chemical Treatment	Effectiveness	Post-Treatment	Remarks
Organo-P Insecticides	25 gpm	None	Caustic Addition	pH to 6 for corrosion control	Ocean disposal	No alternative solution
Carbamates	?	None	Caustic Addition	pH to 7 for corrosion control	Ocean disposal	Incineration contemplated
Triozone Insecticides		None	Acid Pond holdings	pH < 2 for 8 or more hrs.	pH adjustment with lime	
Chlorinated	300 gpm	None	Limestone ditch neutralization	pH 5.5	None	

Source: Plant Interviews.

Table 19. Ozonation of Dehydrochlorination (DHC) Wastes

Sample Designation	Wastewater	pH	Ozone passed through soln. (m-moles)	Ozone absorbed		Ozone Absorption Efficiency (%)	COD raw waste (mg/l)	COD effluent (mg/l)	COD reduction (%)
				m-moles	(mg/l)				
I-18	DHC	12.2	2.07	2.07	994	100.0	3340	1410*	57.8
I-06	DHC	Unadj.-12.6	5.52	5.28	2530	95.6	3340	900	73.0
I-14	DHC	"	8.33	8.18	3920	98.1	3340	745*	77.5
I-12	DHC	"	10.05	9.66	4640	96.1	3340	450	86.5
I-15	DHC	"	12.50	11.26	5400	90.1	3340	314*	90.5
I-11	DHC	adj. - 7.0	6.36	5.62	2700	88.4	3340	1460*	56.5
I-17	Wash Belt	7.8	2.07	1.08	518	52.1	3072	900	70.1

*Sample analyzed immediately following ozonation.

DHC = Wastes from Dehydrochlorination Unit.

Source: Ford and Eckenfelder, 1968.

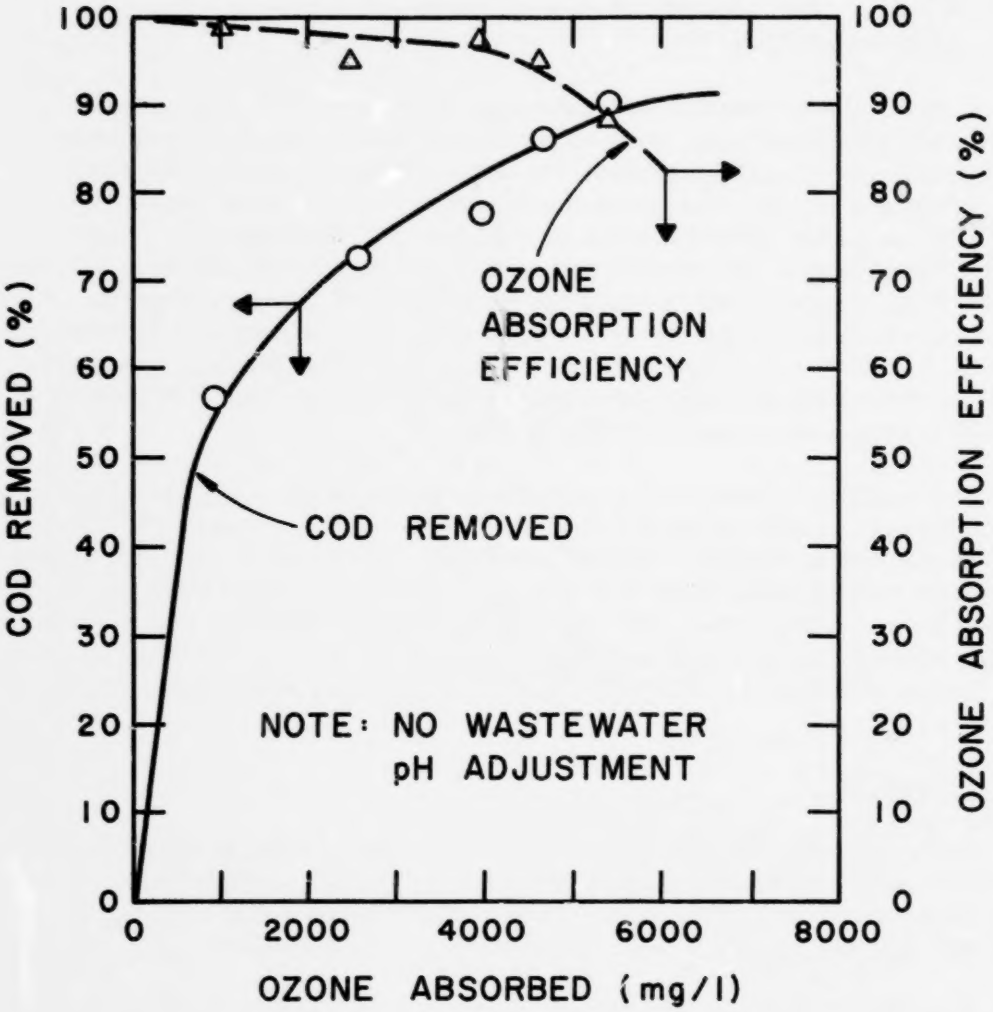


Figure 27. Ozonation Test Results of Dehydrochlorination (DHC) Wastewaters.

Source: Ford and Eckenfelder, 1968.

acid mediums. Catalysts such as ferric chloride greatly increase the hydrolysis rates. The stability of several major pesticides in alkaline mediums is given in Table 20.

In many plants caustic or waste caustic from other operations is used only for pH adjustment, prior to biological waste treatment or chemical coagulation. Chemical degradation occurs to some extent, but the pH levels remain too low and the detention time in the mixing basins is normally too short for detoxification to safe levels. For example, chlorincated hydrocarbon waste neutralized in a limestone trench and held at a pH of 7.2 in an equalization basin for an average of 12 hours showed little reduction in active compounds. Similarly, a plant engineer reported that pH of 7.8 to 8.3 in a neutralization basin preceding biological treatment reduced the concentration of organophosphate insecticides by less than 5% during the two hour detention period.

The addition of sodium hypochlorite solution or gaseous chlorine to herbicidal wastes until a residual chlorine level is achieved can effectively degrade the aqueous stream. The pH levels should be low (3) and the design contact time should be at least 10 minutes at high temperatures (85°F) or longer at lower temperatures. An industry using this technique reports satisfactory results and no major equipment problems to date. Chlorine to phenol ratios in excess of 50:1 may be required to complete the oxidation.

Physical Treatment

Table 21 summarizes the information obtained during plant site interviews. Since pesticide wastes include a broad spectrum of water quality parameters, the physical treatment schemes are quite varied. Design and operating criteria were not available in most cases.

Suspended solids offer little problem in most pesticide manufacturing operations. These operations produce waste streams containing elemental sulfur bicarbonates, sulfates, phosphates, nitrates and other inorganic ions. In general, the salts produced will remain in solution. However, the addition of lime for neutralization can produce insoluble compounds which will precipitate. This sedimentation may occur in the mixing basin if adequate turbulence is not supplied. Often dead spaces occur in mixing tanks and invariably cause problems from sludge bank buildups. If effective sedimentation is desired, long detention times are necessary since the floc produced in typical pesticide wastewater settles slowly. For example,

Table 20. Chemical Treatment

Pesticide	Acid	Alkali	Chlorination
Aldrin	Reaction-HCl	Stable	No Reaction
Dieldrin	Reaction-HCl	Stable	"
Endrin	Reaction-HCl	Stable	"
DDT	Stable	Decomposes	"
Toxaphene	Stable	Decomposes	"
Organic Phosphates		Break Down	"
Carbaryl (Sevin)		Decomposes	"
IPC		Decomposes	"
Chloro IPC		Decomposes	"
Phenoxy Herbicides			Decomposes

Source: Waste Disposal Manual, National Agr. Chemical Association, Washington, D.C.

Table 21. Physical Treatment

Type of Product	Waste Flow	Pretreatment	Physical Treatment	Effectiveness	Post-Treatment	Remarks
Chlorinated Herbicides	30 gpm	pH adjustment to 3 w/ H_2SO_4	Carbon Adsorption in packed tower	95% Phenol 80% BOD removal	Trickling Filter Activated Sludge	
Chlorinated Insecticides Pesticides	1500-3000 gpm	Lime addition	Sedimentation	60% suspended solids removal	None	100-300 ppm chlorinated hydrocarbons in effluent
Chlorinated Insecticides	?	None	Filtration Diatomaceous earth	< 2 ppm as DDT in effluent	Activated Carbon	Concentrated wastes only
Chlorinated Insecticides	?	Filtration	Activated Carbon	< 0.5 ppm as DDT in effluent	Sanitary Sewer	Concentrated wastes only
Formulated Chlorinated Insecticides and Herbicides	Low	None	Sedimentation of Clay Carrier	?	Total evaporation	Solids recycled

Table 21. (Continued)

Type of Product	Waste Flow	Pretreatment	Physical Treatment	Effectiveness	Post-Treatment	Remarks
Organo-P Insecticides	100 gpm	Lime addition	Sedimentation, 2 day detention	10% Suspended solids reduction	None	Milky white effluent $pH = 4$
Organo-P Insecticides	Low	None	5.25% sodium hypochlorite 2:1 dose	100% hydrolysis	None	30 minutes at 212°F 24 hours at 90°F
Triazine Herbicides	Low	HCl added to $pH < 1$	Heat to 150°F for 2 hours	?	pH adjustment	
Organo-P Insecticides		None	Sedimentation, three day detention	Effluent S.S. =900mg/l	None	Pilot studies underway for biological treatment
Metallic Carbamates	High	None	Sedimentation, short	Solids reduced to 1200 ppm from 1600 ppm	Sanitary Sewer	High Na_2SO_4 and other metal surfates

Table 21. (Continued)

Type of Product	Waste Flow	Pretreatment	Physical Treatment	Effectiveness	Post-Treatment	Remarks
Dithiocarbamate Pesticides	28 gpm	None	Dilution by discharge during high flow periods		None	To be discontinued in the near future
Formulated Chlorinated & Organo Phosphorous Pesticides	20 gpm	None	Solar evaporation		None	Low sludge production Dredging landfilled periodically
Chlorinated Sulfur Fungicide	48 gpm	None	Solar evaporation		None	Design rate 2.0 gpm per acid

Source: Plant Interviews.

lime added to one organophosphate pesticide waste produces a milky white suspension in the waste. Only 30 percent of this material can be removed in a lagoon with three days detention. Conversely a chlorinated herbicide plant obtains relatively good removal (up to 30%) of 2,4-D and 2,4,5-T acids, amines and other salts with lime floc. pH adjustment to 6.5 and 12 hours sedimentation is required. The esters are not removed by this technique.

Sludge removal can be accomplished with mechanical scrapers if the sedimentation basin has a regular geometric shape, or it must be done manually if the basin is an irregular pond. Manually cleaned basins are most often used since sludge production rates are small. However, in some cases, sludge volume buildup has been underestimated and the sedimentation basin quickly becomes useless without frequent cleaning. Therefore, accurate estimates of sludge production are important. For example, if lime ($Ca(OH)_2$) is used to neutralize a waste containing sulfuric acid, 1.39 pounds of calcium sulfate will be produced for each pound of sulfuric acid neutralized.

$$\underset{\text{1 pound}}{H_2SO_4} + \underset{\text{1.35 pounds}}{Ca(OH)_2} \longrightarrow \underset{\text{1.39 pounds}}{CaSO_4} + 2H_2O$$

If this material concentrates to a 5% solids sludge in the sedimentation or neutralization tank, it will occupy a volume equal to 28.5 ft^3 per ton. Therefore, one million gallons of waste containing 415 mg/l H_2SO_4 (2000 pounds per million gallons) will produce 2780 pounds of sludge when neutralized with 100% reactive lime. This sludge will occupy 40 cubic feet in the sedimentation basin. If less reactive limestone is used, the sludge production rate is of course higher.

Biological Treatment

Biological treatment of aqueous wastes from pesticide manufacturing processes can be an economical method of reducing toxicity, organic content, and suspended materials. The biological systems used must be carefully cultured in the proper environment to produce specialized organisms capable of utilizing the waste components as food sources, and these organisms must be protected against shock loads, rapid pH changes and poisonings from plant upsets, spills, etc. In order to design and operate a successful biological system, the waste stream characteristics and the limitations of the organisms cultured must be considered. The following discussion will deal with some of the special design considerations that should be included, and design and operating parameters from several existing treatment facilities will be cited. Table 22 summarizes the information on current biological treatment practices obtained during the plant site interviews.

Basic Requirements

Biological populations can be utilized to rapidly and efficiently remove organic materials from waters if a suitable environment is provided. For aerobic (full oxygen based) biological proliferation, adequate food, oxygen, nutrients and proper pH and temperature conditions are required.

Temperature: The temperature effects on biological systems are significant, even at ambient levels around the United States. During the hot summer months, biological activity is accelerated and oxygen solubility is decreased, presenting the critical design situation for aeration equipment. During the winter months biological activity decreases with temperature as does the removal rate of organic material. Therefore, winter conditions should be used as the initial design situation for determining the size of the oxidation reactors. Figure 28 indicates the magnitude of the effect that normal winter temperatures may have on soluble industrial wastes. These studies conducted in the Northeastern United States show that temperature effects should be considered in a treatment system design. Even though biological systems operate most efficiently at temperatures in the 30° to 35°C range (40° to 45°C for certain thermophilic bacteria), systems to maintain temperatures near the optimum level are not usually feasible for industrial wastes because of the added expense. The system size and detention time is usually increased to compensate for reduced biological activity during cold weather.

pH: Biological systems may operate reasonably well in the pH range from 5 to 9 if adequate acclimation time is allowed and rapid pH changes do not occur. Most biological systems are designed to operate in the 6 to 8 pH range. Rapid pH changes are extremely detrimental to biological systems and must be prevented. The aeration system acts as a well mixed equalization tank capable of reducing the effect of shock loads, especially if the power level is high enough to insure complete mixing in the basin, but the system capabilities can be exceeded. The

Table 22. Biological Treatment

Type of Product	Waste Volume	Pretreatment	Biological System	Design Parameters	Effectiveness (Reported)	Post-Treatment
Chlorinated Herbicides	2 mgd	pH adjustment 5:1 dilution with cooling water - nutrient addition	Trickling filter	2.5#Phenol 1000 ft^3/day 675 gpd/ft^2	70% phenol removal	Activated sludge
Chlorinated Herbicides	2 mgd	5:1 dilution nutrient addition & trickling filter	Activated sludge	6 hr./aeration MLVSS = 600 mg/l	95% phenol removal	None
Chlorinated Herbicides	85,000 gpd	30:1 dilution with sanitary sewage	Trickling filter (one third of diluted flow only)	3300 gpd/ft^2 25#BOD/1000 ft^3/day; 0.5# phenol/1000 ft^3/day (operated at less than design loading	70% BOD, 55% phenol, 0% phenoxy acid removal	Aerated lagoon and stabilization pond

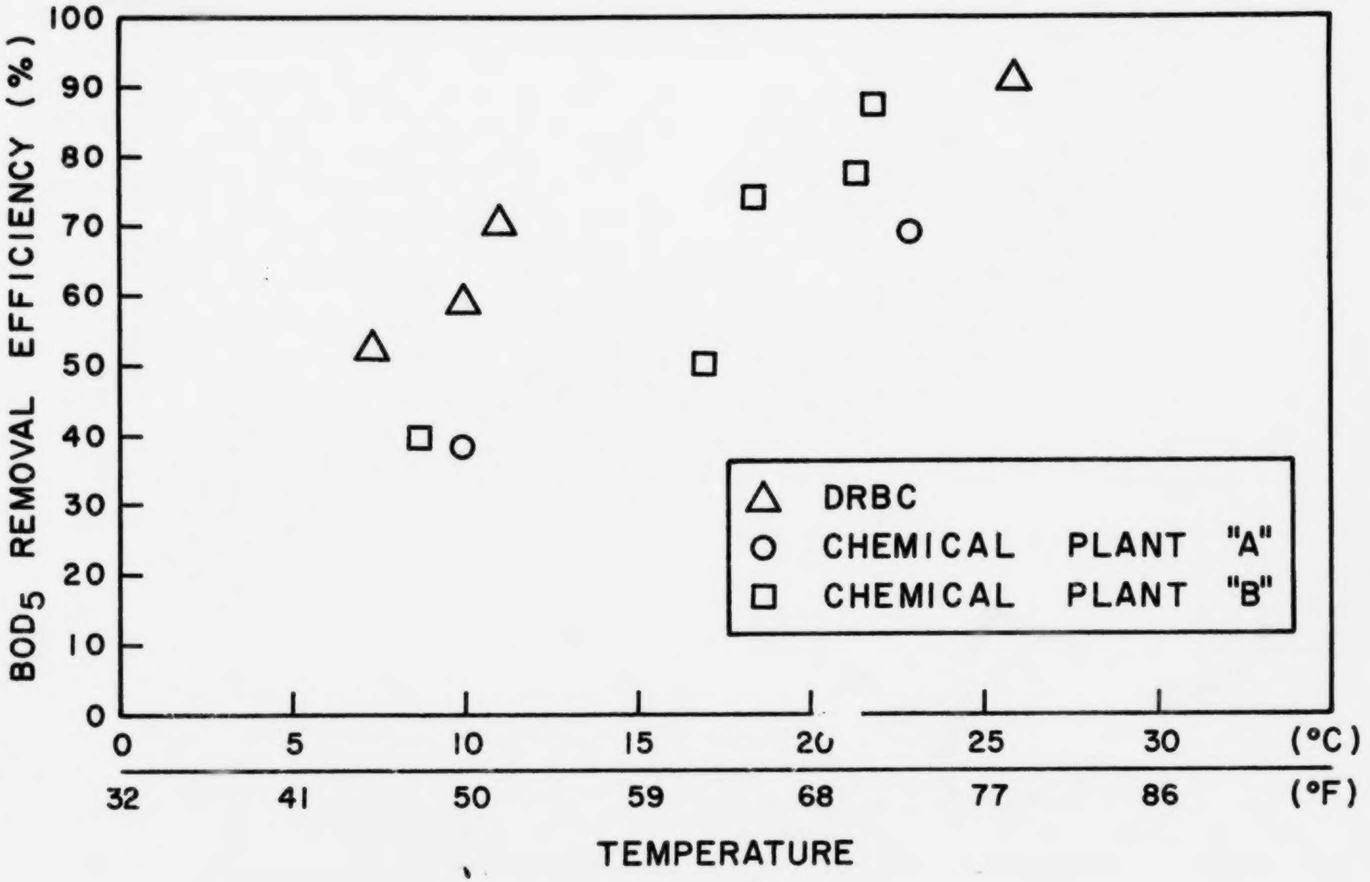
Table 22, (Continued)

Type of Product	Waste Volume	Pretreatment	Biological System	Design Parameters	Effectiveness (Reported)	Post-Treatment
Chlorinated Herbicides	85,000 gpd	30:1 dilution + 1/3 of flow passes through trickling filter	Aerated lagoon	3 days detention, 2500 #BOD/acre/day 23,900 #O_2/day, MLVSS= 200 mg/l	70% BOD, 75% phenol, 55% phenoxy acid removal	Stabilization pond
Chlorinated Herbicides	85,000 gpd	30:1 dilution aerated lagoon	Stabilization pond	30 days detention, 30 #BOD/acre/day	50% BOD, 50% phenol, 25% phenoxy acid removal	None
Chlorinated Herbicides	43,000 gpd	Carbon adsorption and pH adjustment	Trickling filter	30 gpd/ft^2 .07 #BOD/1000 ft^3/day	90% phenol removal, 70% BOD removal	Activated sludge
Chlorinated Hydrocarbons	43,000 gpd	Carbon adsorption & trickling filter	Activated sludge	16 hr. aeration 2 pounds BOD/1000 ft^3/day	46% phenol 44% BOD removal	None

Table 22. (Continued)

Type of Product	Waste Volume	Pretreatment	Biological System	Design Parameters	Effectiveness (Reported)	Post-Treatment
Organo-P Insecticides	720,000 gpd	pH adjustment with lime	Activated sludge	6 days aeration, 27 #COD/1000ft^3/day MLVSS 6000 mg/l D.O. > 2	99% BOD 96% COD 99% OP removal	Municipal Sewer
Carbamate Insecticides	High	pH adjustment	Aerated lagoon	?	Good	Some toxic wastes bypass lagoon and are barged to sea

Source: Plant Interviews.



NOTE

1. ALL LOADINGS ≈ 0.5 lb BOD_5 applied / day / lb MLVSS.
2. ACTIVATED SLUDGE TREATMENT OF WASTEWATERS DISCHARGED FROM CHEMICAL PLANTS.
3. GOOD SLUDGE SETTLING OBSERVED AT COLDER TEMPERATURES.

Figure 28. The Effects of Temperature on BOD Removal from Soluble Industrial Wastes.

Source: Ford, 1971.

natural buffering capacity (perhaps as high as 0.7 pounds of alkalinity equivalent per pound of COD removed) is not sufficient to protect the system against large strongly basic slugs of waste and offers no protection against acid slugs. The CO_2 produced in carbon bio-oxidation can affect the pH of the system. CO_2 tends to cause slightly acid conditions in high rate systems. In addition, biological systems can produce acid byproducts such as H_2SO_4, HNO_3, and H_3PO_4 from the oxidation of pesticidal components such as ethyl parathion. Adequate buffer capacity must be provided to prevent significant pH changes.

Nutrients: In addition to organic substrate, biological populations require inorganic nutrients for cell synthesis, including nitrogen, phosphorus, iron, silica, and others. Most of the required trace elements are present in sufficient quantities in pesticide manufacturing wastewater streams, with the exception of nitrogen and/or phosphorus in some cases. In general, a carbon to nitrogen to phosphorus ratio of 100:5:1 is adequate to allow unrestricted biological growth. If these nutrients are lacking, they should be added to the waste stream. Ammonia or soluble nitrates and nitrites can be added to overcome nitrogen deficiencies, and soluble phosphates can be added as a source of useable phosphorus. These additions will seldom be needed for pesticide manufacturing wastes, and when they are, waste streams from other plant operations can often by used to supply the needed nutrients.

Degradability: Almost every organic compound can be broken down biologically if proper environmental conditions are maintained and sufficient time is provided. Organisms must be allowed adequate time to develop the enzymes necessary to stabilize the waste components for energy and cellular building material. After acclimation, the organisms will consume the wastes at a rate dependent on many factors. If this utilization rate is slow, the waste may be considered non-biodegradable for practical treatment purposes. Compounds such as tertiary aliphatic alcohols, ethers, benzene, trichlorophenols and pentachlorophenols fall into this refractory group and present problems in pesticide waste treatment. Some of the factors which affect biodegradability are:

1. Solubility and availability: Compounds in emulsified or chelated forms are not readily available to micro-organisms and are slowly removed. A prime example is DDT and many of its isomers which are extremely insoluble in water.

2. Molecular size: The physical size of complex molecules often limits the approach of enzymes and reduces the rate at which organisms can break down the compound. Many pesticide compounds and their isomers are of large and complex structure making them resistant to degradation. Some carbamates and carboxylic acid based compounds are examples.

3. Molecular structure: Aliphatic (straight and cyclic) compounds are in general more degradable than aromatic compounds. Thus some pesticide compounds and parts of some molecules can be degraded easily while other parts cannot. In some cases, partial degradation will occur, but the pesticidal activity of the waste stream may not be reduced significantly if the toxic components of the compound are bioresistant.

4. Substitutions: The substitution of elements other than carbon in the molecular chain often make the compound more resistant. Esters and epoxides, salts, etc. are more resistant than the base pesticidal compound.

5. Functional Groups: Halogen substitution to an aromatic compound renders it less degradable. The number of substitutions and the location are of importance. Chlorophenols are an excellent example of increasing resistance with increasing substitution. Amino and hydroxyl substitutions often increase degradability.

Most pesticide manufacturing wastes are susceptible to some degree of biological treatment, but in special cases 10 to 15 days of contact are required to achieve significant removal. Therefore, a detailed study of the waste properties, and biodegradation tests are necessary before a biological treatment method is chosen and designed.

The biological methods commonly used in pesticide manufacturing waste treatment include:

1. Trickling filters; normally high rate systems used as roughing filters.

2. Activated sludge; usually highly active biological solids, extended contact systems.

3. Aerated lagoons; long detention lower biological activity basins equipped with surface aeration equipment.

4. Stabilization ponds; long detention low biological activity basins with no aeration facilities. These systems are usually facultative. They are most often used as polishing devices to remove small amounts of organic material. The suspended solids in the effluent are usually higher than the influent suspended solids since biological floc and algae are present in the effluent.

Trickling Filters

Trickling filters are often used in industrial waste systems because of their ability to handle fluctuating waste loads and toxic "slugs" without longterm upset. These systems are used as "roughing filters" or load leveling devices. After passage through the filter, the waste stream organic load is reduced (up to 85% BOD reduction for some one-pass systems) and shock loads or toxic slugs are attenuated by mixing. If recirculation is employed, further organic removal and load leveling is achieved.

The typical filter system consists of a bed 8-10 feet deep composed of 2-4" diameter stones. Biological slimes attach themselves to the rock surfaces and consume the soluble wastes as the wastewaters trickle over the stones. Natural draft or forced air ventilation from the underdrains through the bed, counter current to the wastewater flow, is required to keep the system odor free. Improved operation can be achieved in special cases if synthetic polyethylene media are used instead of rock. Well-designed media reduce the possibility of plugging and increase ventilation, thus allowing very deep trickling filters to be used. Filters carrying synthetic media in excess of twenty feet thick are now being used effectively for some wastes.

As the soluble components of wastes are utilized by the organisms in a filter bed, the slime layer builds up and eventually sloughs off. If a toxic slug reaches the filter, the outer layer of organisms will contact the toxic material and will die. The dead material will slough, exposing new and active organisms which will continue to utilize the waste once the toxic material has passed through the system. If the system is overloaded, the excess organic material will also pass through the system, not affecting the biological processes. Thus the trickling filter is a good pretreatment device (roughing filter) for the types of loads which can occur in pesticide manufacturing. If recirculation is employed, wastes with high organic loads can be treated.

Normally hydraulic loadings on trickling filter systems should not exceed 0.5 gallons of waste per minute per square foot of filter surface. For "roughing filter" operation, organic loading is relatively unimportant. However, the loading should be high enough to efficiently utilize the organisms for waste removal. A chlorinated herbicide plant reports that loadings of 25 pounds BOD per day per 1000 ft^3 of filter volume at flow rates of 0.11 gpm/ft^2 resulted in 70% removal of phenol wastes and 80% reduction of BOD for a one pass roughing filter system. In this system the wastes were mixed (1 to 6) with cooling waters for dissolved salts and phenol dilution before treatment. After one pass through the filter the phenol wastes received final treatment by activated sludge.

Similarly, a conventional trickling filter treating chlorinated herbicide wastes diluted approximately 30:1 with municipal sewate showed 72% reduction of BOD and 54% reduction of chlorophenols, but no removal of chlorophenoxyacids. This filter was operated at a hydraulic loading of 0.24 gpm/ft^2 and an organic loading of 45 #/1000 ft^3/day.

New, high rate filters with synthetic media may be utilized for pesticide waste treatment in the future. However, since some dilution is required for many pesticide manufacturing wastes to reduce toxicity and dissolved salts before biological treatment, the resulting organic concentration is too low to sustain high rate filters. For this reason these systems should be considered only in specialized cases.

Activated Sludge

Activated sludge treatment is the biological oxidation of wastes in a fluidized reactor containing a concentrated biomass supplied with organic waste and oxygen in correct proportions to stimulate efficient utilization of the waste by the organisms for energy and microbial cell synthesis. After sufficient contact, the wastewater (mixed liquor) is drawn off and the bacteria are allowed to coagulate and settle in a clarifier. The settled "sludge" is returned to the system to maintain a high bacterial population in the aeration basin, or wasted when the sludge production exceeds the system's requirements. The clarified water is released. In this process, suspended and dissolved organic material is converted to biomass which can be removed by sedimentation. Most organics can be utilized by the bacteria, including pesticides, pesticidal isomers, solvents and organic by-products under proper conditions. The utilization rates are different for each compound so removal efficiencies can differ for the various types of compounds in the system.

Activated sludge systems for the treatment of pesticide manufacturing wastes may carry unusually high solids (bacterial) concentrations in the aeration basin. A conventional activated sludge system for municipal sewage will usually maintain a mixed liquor suspended solids loading of 2000 to 2500 mg/l in the aeration tank. Pesticide waste systems may maintain suspended solids loadings as high as 18,000 mg/l with perhaps 1/3 of these solids active. If lime is used for neutralization, calcium carbonate, calcium sulfate, and calcium phosphate will form a major portion of the fixed solids.

In one organophosphorus pesticide plant, the waste is treated by a modified activated sludge process. The waste is held in an aeration basin for six days to achieve 95 to 99% reduction of pesticidal compounds. BOD removals in excess of 99% are also achieved. Mixed liquor volatile solids levels of 5000 to 6000 mg/l (total solids often exceed 15,000 mg/l) are maintained and dissolved oxygen levels of 2 mg/l or more in the aeration basin are provided by an automatic oxygen monitoring system which controls the blowers. The waste and returned sludge are introduced into the aeration tanks at several points to help provide good mixing. This in conjunction with an adequate mixing power level serves to protect the system design. COD loading of 12,000 pounds per day (0.08 #COD/day/#MLVSS) and air flows up to 24,000 cfm are used as operating parameters. Efficiencies of 99% BOD removal, 96% COD removal and 99% organophosphorus removal are reported. The system is extremely sensitive to the organic loading rate and operates poorly if the proper COD loading is not maintained. Sludge production of 300 pounds of dry solids per day (.025 #/#COD removed) is typical. The clarified effluent and excess biological solids are sent to conventional activated sludge municipal treatment plant for final treatment.

An activated sludge system presently used to treat a chlorinated hydrocarbon herbicide waste is of a more conventional nature. The process waste is first diluted 5:1 with low BOD, nontoxic cooling waters and ammonia is added to satisfy nutrient requirements. The waste stream is then passed through the "roughing filter". After one pass, the filter effluent flows into an aeration basin for six hours of contact with a biological culture maintained at 600 mg/l mixed liquor volatile suspended (MLVSS) solids. The waste is introduced at the head of the basin only, since the filter serves to prevent shock loads. The initial phenol levels in the aeration basin often approach 30 mg/l and 95 to 99% removals are reported. The total MLSS level is maintained at 900 mg/l and approximately 2/3 of the solids are classified as volatile. The settling characteristics of the sludge produced by this system are good. The sludge is removed in the clarifier, partially de-watered and disposed of by deep well injection into an unusually permeable underground formation. The system operates well but is subject to periodic upset when unusual toxic compounds enter the system via spills or process upsets. A large holding basin is available into which wastes may be bypassed if toxic components are suspected. The bypassed wastes can then be metered into the treatment system slowly so that dilution will reduce the effect of toxic components on the organisms.

Many pesticidal wastes which can be diluted at the manufacturing plant are discharged directly into municipal sewers. Often little pesticide removal occurs. DDT discharged into a large northeastern U.S. municipal plant appears to pass through the system with less than 25% removal. The activated sludge system accounts for little actual biooxidation since most of the removal occurs in the primary sedimentation basin. The DDT content of the effluent is high but sediment samples obtained below the outfall contain relatively large amounts of DDD but little DDT. Thus it appears that little degradation of DDT occurs during the short contact period in the activated sludge plant, but some biological oxidation occurs slowly in the river sediments.

Studies conducted in England also show that some pesticide removal occurs in a municipal treatment system, but that high effluent concentration can also occur. The following statements are obtained from "Notes on Water Pollution Research" (March 1967), published by the Water Pollution Research Laboratory, Stevenage, England:

> "The Laboratory has carried out a limited survey of pesticides entering and leaving the works mentioned above, which treats, by biological filtration, sewage from an area containing a factory at which pesticides are formulated. Dieldrin, α-BHC, γ-BHC, and DDT were all present in the crude sewage. The number of results was not sufficient for the calculation of a materials balance but it is clear from the results that all four

> pesticides tend to concentrate in the primary and filter sludges. For example, the concentrations of γ-BHC in composite samples of sewage for five consecutive days varied from 1.3 to 64 μg/l but on the same days the concentration in the primary sludge was of the order of 300 μg/l. A similar relationship was found for dieldrin. DDT was present in the crude sewage but during sewage treatment it was largely broken down to DDE and TDE, both of which were present in the primary sludge. Pesticides were present in the filter sludge (total solids content approximately four percent) at concentrations of some hundreds of micrograms per litre and in three samples the amounts of DDE were greater than 1 mg/l.
>
> "The final effluent contained about 1 μg/l of γ-BHC throughout the period but the other pesticides were present at markedly reduced concentrations. Fish kept in a cage within the effluent channel remained alive during the seven-day period of the experiment."

Aerated Lagoon

In situations where land is available and a low maintenance, low operational expense system is desirable, the aerated lagoon is an attractive treatment method. Aerated lagoons are not generally effective for treating highly concentrated wastes, i.e., COD >700 mg/l. The system normally employs surface aeration equipment on a 6 to 10 foot deep basin with several days detention. No sludge return is employed, so that suspended solids levels (biological solids) are low, thus necessitating long detention requirements for pesticidal wastes. Aerated lagoon loadings of 25 to 50 pounds of BOD per acre per day are low enough to prevent anaerobic conditions in a well aerated and well mixed system, and may be design criteria usable for pesticidal wastes if the toxic compounds are not extremely bioresistant.

In one system operated on an experimental basis, a chlorinated hydrocarbon herbicide waste was diluted 30 to 1 with municipal sewage and fed at an average BOD rate of 615 pounds per acre per day, and 70% BOD removal was obtained. Twenty-three thousand nine hundred pounds of oxygen transfer capacity per day were provided by four surface aerators (125 horsepower). Phenolic loadings of 29 pounds per acre per day (1/3 phenol, 2/3 phenoxy acids) were maintained and the system achieved 80-90% phenol removal and 56 to 72% phenoxy acid removal. The average detention time was slightly more than three days. Low biological solids levels were noted in the basin. During one four month sampling period (summer), effluent suspended solids averaged 108 mg/l and the settleable solids averaged 5.3 ml/l. Effluent BOD levels averaged 26 mg/l and phenol levels were 0.2 mg/l. Phenoxy acids were unreported but probably approached 1.7 mg/l in the effluent.

In general effluent quality from an aerated lagoon is poor because the biological solids present in the overflow exert a BOD. However, the breakdown of toxic organics may be nearly complete with almost no pesticidal agents in the effluent (EPA Report in press, Grant # 12130 EGK 06-71). To accomplish this, long detention times will be required due to the inherently slow biological utilization of complex hydrocarbons. One particularly difficult waste (a combination of pesticidal and petrochemical process effluents) is presently being treated by aeration in a lagoon, having a detention time of seventeen days. Pesticide levels in the effluent are low, but COD and color remain high. Plant officials feel that if more air can be supplied to the system, higher organic removals can be capable of maintaining dissolved solids levels of approximately 2.0 mg/l in the entire system. Higher D.O. levels do not significantly increase oxidation rates, but D.O. levels less than 0.5 may be inhibitory (Ford, 1971).

Stabilization Ponds

An additional biological treatment system which is used as a polishing device in most instances and a complete system in some cases, is the stabilization pond. The pond acts as a reactor where biological oxidation is allowed to proceed at natural rates. The ponds are normally designed to be facultative, with aerobic conditions near the surface and anaerobic conditions in the bottom waters. The anaerobic organisms can successfully metabolize many relative resistance compounds but often produce odors in the process. Therefore, the aerobic conditions must be maintained in the surface waters to reduce or elimate the odors which are by-products of anaerobic digestion.

The success of treatment is dependent upon the proper balance of bacterial and algal activity in the system since the former utilize organic wastes for energy and the latter produce oxygen in the presence of sun light.

Excessive organic loadings, low temperatures, rapid or severe pH changes, toxic compounds and high concentrations of sulfur-containing compounds can cause significant reductions in treatment efficiencies.

The long detention times normally utilized in stabilization pond design gives microorganisms the time to degrade relatively resistant compounds. If organic loadings are low enough to insure aerobic conditions, at least in the surface waters, good BOD and COD reductions can be achieved in relatively short time periods (1-3 days) but phenols, phenolic acids and complex hydrocarbons will remain. The operators of an existing pond with a 20-day detention period claim the BOD is reduced from 120 to near 0 mg/l (sic), the sulfides are reduced from 15 to near 0 mg/l and total phenols are reduced from 17 to approximately 7 mg/l under summer conditions. It is unusual for stabilization pond effluents to have such low BOD levels since the algae and bacterial solids in the effluent will exert a BOD. Biological oxygen demands in excess of 10 mg/l are more typical. In another system an existing polishing pond following an aerated lagoon reduces chlorophenols from average levels of .33 to .12 mg/l and phenoxy acids from 1.62 to 1.27 mg/l in a 30-day detention period. BOD reductions from 23.1 to 14 mg/l are typical in this system.

Since algal growth is of major importance in a system of this type, wastes with high color content, high turbidity or emulsions cannot be treated effectively. The light penetration may be so reduced by these conditions that good algal growth (and the associated oxygen production) is impossible. Likewise high sulfur containing wastes often result in the proliferation of dark bacterial cultures which effectively prevent light transmissions and reduce removal efficiencies (FWPCA Report, 1970).

As indicated earlier, a properly designed pond can produce good effluents. Detention times of 20 days or more are typical. Organic loading should be relatively low for pesticidal wastes, perhaps in the range of 20 to 30 pounds of BOD per acre per day. Care must be taken to eliminate algal toxins, high sulfur wastes and excessive turbidity. If possible pilot scale units should be run to obtain usable design information on a particular waste before the pond system is constructed.

Incineration

High temperature incineration is the waste disposal method preferred by the majority of plant managers interviewed. A well-designed, well-operated system can handle a wide variety of wastes without upsets and produce a residue that is small in volume (if present at all), and void of pesticidal components. Gaseous, liquid and solid pesticidal wastes may be burned in incinerators. Table 23 contains a summary of the information on incineration techniques gained during the site interviews.

Incinerator design is important in insuring that complete destruction of pesticides and related compounds occurs. The burning chamber must be designed to provide:

a. Adequate residence time in the flame
b. Adequate mixing to insure contact of the waste with the necessary amount of oxygen
c. Adequate oxygen in the burning chamber for complete combustion plus a small amount of excess air for safety
d. Adequate temperature to insure complete destruction of the organic compounds.

Several types of incinerators are available which can provide the proper burning conditions. These include multi-chamber types, tangentially fired vortex type burners, baffled chamber burners, and fluidized bed burners. Each type has some advantages and disadvantages for various types of wastes. Some general considerations will be discussed below.

The residence time in the flame can be controlled by properly sizing the primary burning chamber and the fuel and air flow rates. The chamber should provide a minimum of 0.3 to 0.5 second residence time at normal burning temperature of 1400 to 1800°F. At higher temperatures, oxidation occurs more rapidly and shorter residence times can be tolerated.

Mixing is controlled by the air-fuel injection into the chamber. High pressure nozzles and baffle plates are often used to disperse liquid and gas streams into the primary combustion air. Moving jets which oscillate spraying the waste against a dispersion plate have also been used successfully. If auxiliary fuel is used to maintain high burning temperatures, the fuel stream can be used to aid in dispersing the incoming waste stream. At high temperatures many relatively noncorrosive fluids become highly corrosive (i.e. toluene) and the nozzle and baffle plate design should consider this factor.

Table 23. Incineration

Type of Product	Waste Burned	Pretreatment	Incinerator Type	Operating Characteristics	Air Pollution Control	Remarks
Organo-P Insecticides	All liquid wastes; 4% organics 1.5% organo-P	None	Atomizer Burner Natural gas fuel	1600°F	None	P_2O_5 particulate and high SO_2 present
Organo-P Insecticides	Gaseous wastes only - Mercaptans	None	Thermal Oxidizer, Natural Gas Fuel	1800°F For odors only	None	No detectable odor. High fuel costs
Chlorinated Pesticides	Tank and still bottoms-high chlorine wastes	None	Vortex burner, Natural gas fuel available but not used	1400°F	23 foot packed tower scrubber carrying 2" saddles, 500 gpm	Persistent white plume resulting from sodium chloride aerosol. Scrubber water contains 300-400 ppm HCl
Organo-P Insecticides	Gaseous wastes, concentrated liquid semi-solid wastes	None	Atomizer Burner, Natural gas fuel	1600°F For odors & liquids	Caustic spray fiber-glass demisters	Persistent white plume from P_2O_5; SO_2 present

Table 23. (Continued)

Type of Product	Waste Burned	Pretreatment	Incinerator Type	Operating Characteristics	Air Pollution Control	Remarks
Chlorinated Herbicides	Concentrated chlorinated wastes and general petrochemical process wastes	Blending	High pressure atomizer, natural gas available	Horizontal combustion chambers 1800°F	Venturi scrubber 18" drop	Very satisfactory services reported
Carbamates Urea Based Insecticides	All process wastes	Blending	Low pressure spray against baffle plate	1400°F	None	No problems reported
Chlorinated Insecticides	Concentrated chlorinated residues	Screening and blending	Down flow primary burner	1000-1400°F Steam injected	Carbon block packed scrubber	Primary air preheated by exhaust

Table 23. (Continued)

Type of Product	Waste Burned	Pretreatment	Incinerator Type	Operating Characteristics	Air Pollution Control	Remarks
Chlorinated Insecticides	Gaseous wastes-methyl chloride	None	Low Pressure natural gas burner	1500°F	Dilute caustic packed tower scrubber	99% removal of HCl
Urea Herbicides	Veracil	None			None	
Chlorinated Surfur Fungicide	Toluene & Methanol waste stream containing some product & off gas stream frcm product drying	None	High pressure stream atomizer, natural gas aux. fuel	1700°F	Packed tower caustic scrubber for HCl	A dense white water vapor plume is formed. Particulates seldom exceed Ringelmann No. 1

Source: Plant Interviews.

The oxygen supply to the primary burning chamber is of prime importance. Underfire air, or air which enters the flame area, influences mixing, oxidation and burning temperature. Too much air causes a cooling of the flame and reduced residence time; too little air produces incomplete combustion, inadequate mixing and, at times, excessive temperatures. Secondary air, or air introduced beyond the primary flame area, is required to insure complete oxidation of the gases as they leave the flame area. The exhaust temperature can be controlled by the secondary air rate. Preliminary studies indicate that, for best burning of typical pesticidal wastes, primary air rates should exceed the secondary air rates to provide exhaust gases with the least amount of toxic components, including SO_2 and CO.

Most operators agree the combustion temperature in the incinerator should be maintained in the 1400° to 1800°F range. In some special cases, high temperatures may be required, but most wastes will be destroyed at these temperatures. The combustion temperature may be controlled in a number of ways. Good insulation will increase the combustion temperature of a furnace; proper air-fuel control and proper primary to secondary air ratios will increase burning temperatures; auxiliary fuels can be used to increase burning temperatures; steam injection and preheating of combustion air or the waste stream itself will raise burning temperatures. Although high burning temperatures insure better oxidation of the waste stream, excessive temperature levels are not recommended. As the burning temperature increases, the resistance to oxidation of the materials used to construct the furnace decreases, and incinerator costs increase. Noxious gases, notably oxides of nitrogen, increase markedly in concentration as the combustion temperature increases. In addition, inorganic salts, including NaCl and P_2O_5, are produced in smaller and smaller sized particles as the temperature increases. These aerosols may act as nuclei for droplet formation and produce persistent white fogs when humid conditions exist. Even complete combustion will not eliminate aerosol formation, but the severity and persistence of the resulting plumes can be reduced with proper burning.

Pesticide wastes containing sulfur compounds, chlorine, chlorides, phosphorus, flourides and heavy metals will produce airborne emissions that require the use of air pollution control devices. In order to burn compounds containing the constituents listed above without violating federal or state emission standards, incinerators are normally equipped with a scrubber. These devices are widely accepted because they can be used to control acid gases and particulates, they are corrosion resistant and reliable.

Scrubbers may be grouped in two basic categories, low energy and high energy devices. Low energy scrubbers include packed towers, spray towers, and plate towers. Packed towers consist of deep beds of inert packing material through which air and scrubbing liquids flow. In the counter current type tower, scrubbing liquid flows downward and the exhaust gases flow upward contacting the large wetted areas of the packing. This type of device is excellent for soluble gas removal and effective in removing large particulates. Small particulates such as NaCl crystals are not removed well. A twenty-three foot packed tower carrying 1-1/2" ceramic packing is used to scrub exhaust gases from a chlorinated hydrocarbon waste burner. Water flows up to 500 gpm are used to remove the HCl resulting from the combustion of 2-3 gpm of concentrated waste. The scrubber water collects 300-400 ppm HCl in one pass through the tower. The scrubber water is neutralized before discharge into a receiving stream. The tower, however, is ineffective in removing sodium chloride from the air stream.

Spray scrubbers produce showers of fine droplets with a series of nozzles and the exhaust gas to be cleaned is passed upward through the spray. Particulates are swept out of the air stream, and some soluble gases are removed. Collection efficiencies are low. A spray tower used for organophosphate insecticide wastes was found to be ineffective for aerosol collection (P_2O_5) until a fiberglass demister was installed. The demister has made the spray scrubber system capable of 99%+ removal of particulates and acid gases when a mild caustic is used as the scrubbing liquid.

High energy scrubbers are more efficient as gaseous and particulate removal devices, but they are more expensive to operate. The venturi scrubber is an example of the high energy type of scrubber. The gases are forced through a throat at high velocity and allowed to expand rapidly. Water is injected in the high velocity, high turbulence section, where impaction, condensation, and absorption result in efficient gaseous and particulate removal. A venturi scrubber presently is used to clean the exhaust from a chlorinated hydrocarbon incinerator. The plant engineer reports that it operates well at 18 inches of water pressure drop. No particulate or odor problems have occurred since the scrubber was put into operation. Corrosion has produced some difficulties, but replacement with acid resistant materials has evidently solved these problems. The acidic scrubbing water is mixed with the process waste stream before neutralization and biological treatment.

One additional problem associated with most scrubber systems is the quenching section. When a gas stream enters a scrubber, it is cooled considerably by the scrubbing liquid. However, in the quenching area, both hot gases and the cool liquid contact the chamber walls causing severe stresses in the lining materials. Therefore, considerable thought must be given to quench section design and choice of firebrick.

Tall stacks have often been used to disperse incinerator gases rather than clean them. However, stringent air pollution laws in effect or proposed in almost all states will require gas cleaning, giving no credit for tall stacks. In most cases, tall stacks successfully disperse contaminants, preventing high concentrations from reaching ground level. However, there are instances when stacks do not work well, especially if the plant is located in a valley area or an area of frequent atmospheric stagnation. The plume may persist and reach ground level in concentrated form, rather than being dispersed as expected under normal meteorological conditions. If the plume contains SO_2, HCl mist, phosphoric acid mist or heavy metals, problems can result. Therefore, air cleaning devices are recommended on all pesticide waste incinerators. Scrubbing devices usually saturate the exhaust stream with water vapor producing a plume containing condensed water. These droplets tend to hinder dispersement and further decrease the effectiveness of tall stacks.

Burial as a Disposal Method

Almost every pesticide manufacturing plant contacted during this study utilized burial as a method of waste disposal for some portion of their process waste. In some cases, liquids and semi-solids are buried in containers, but most plants utilize burial for solid wastes only, and cover burial is used in most cases. Several plants employ private disposal companies to collect, transport, and bury their wastes off the plant property. With the exception of one plant (Rima, 1970), no manufacturer had investigated the migration rate or pollution potential of the buried waste. In most cases, care was taken to choose burial sites in relatively impermeable soil, away from ground water and surface water supplies; but actual follow-up studies and site monitoring are not being conducted. However, one plant indicated that they were investigating the possibility of incorporating their lagoon sludge into an asphalt mixture before landfill burial to reduce the possibility of leaching.

Burial rates ranged from 3-4 tons per day of semi-solids contained in 55-gallon steel drums, to hundreds of tons of dredging from a sedimentation lagoon buried over a three day period. All the plants which utilized lagoons had plans to remove the solids from the lagoon when necessary and dispose of them by landfill. No information on drying times, transportation problems or landfill operations was available since records were seldom kept or available for this report. Disposal costs ranged from $6.50 per 55-gallon drum (approximately $32.50 per ton) to near zero costs for on site pit disposal of lagoon sediments. It is virtually impossible to cite typical costs or to describe the effectiveness and safety of a "typical" burial operation.

In general, it is recommended that extreme caution be used when pesticidal waste burial is necessary. Even if a soil analysis is performed and reasonable distances to ground and surface waters are maintained, the possibility of contamination still exists. Pesticide movement in a heterogeneous soil system is a complex phenomenon that is not completely understood. Therefore, adequate design parameters cannot be cited with certainty for all pesticides under all conditions.

In addition, a well-designed and well-constructed landfill is only safe if operated properly. Sloppy waste handling at the site is a significant problem. Several plant managers mentioned poor landfill operation as a major point of concern. Leaky transfer equipment, ruptured or poorly sealed drums, blowing dust and wet weather operation were mentioned as reasons for possible surface contamination at the burial sites.

CHAPTER VII

THE COST OF WASTE TREATMENT

Cost is a major factor considered in waste treatment and disposal system design. However, since equipment requirements, labor costs, operating costs and maintenance expenses are a function of the type plant involved, the housekeeping practices of the plant and the geographic location, the economic parameter is most difficult to qualify. The following discussion will deal in general terms with the economics of several of the major treatment and disposal methods discussed in the literature and specific data from private interviews will be included where possible.

Pesticide manufacturing wastes are basically organic chemical wastes which may be treated in a variety of ways. The toxic components, usual pH range and high dissolved solids levels of pesticide wastes may cause special problems which can increase costs, but in general the treatment costs should parallel those required for other chemical wastes of similar organic loading. Therefore, the generalized cost estimates included in this discussion which are based on municipal and petrochemical treatment history should be viewed as rough estimates which may be somewhat in error.

Photochemical Degradation

Using experimental data for the photochemical degradation of the compounds at 10 cm depth, a cost estimation has been made for a 50% degradation. The estimates are based on power consumption using a cost of $0.015 KWH. Because these cost figures are extrapolated from an experimental situation, actual field application might function less expensively. Attention should be directed to the geometric and reflection aspects of ultra-violet radiation for a more economical process design.

Compound	Cost/Mil Gal
Aldrin	$24.00
Dieldrin	$73.00
Endrin	$57.50

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Activated Carbon

A method of predicting the cost of activated carbon treatment has been developed by Dorr-Oliver, Inc. Treatment cost for low organic wastes, based upon a two-stage counter-current absorption process, can be predicted by the following equations:

Capital Cost:

$$\text{Log (cost)} = -.839 - 0.495 \text{ Log (influent flow)}$$

Operating Cost:

$$\text{Log (cost)} = \frac{1}{0.45 \text{ Log (influent flow)} + 1.06}$$

Total Cost:

$$\text{Log (cost)} = \frac{1}{0.396 \text{ Log (influent flow)} + 0.83}$$

where

Cost = Cents/1000 gal.

Influent Flow = 1000's of gallons

The assumptions behind the development of these equations include:

1) Carbon dosage = 300 mg/l

2) Carbon cost 7 cents per lb.

3) Power cost 1 cent/KWH

4) Steam cost 1 dollar/million BTU

5) Polyelectrolytes cost 1 dollar/lb.

6) Average carbon loss = 5% per cycle

7) Influent flow = 10^6 gal/day

8) Average waste stream COD = 40 mg/l

9) Maintenance was assumed at 3% of fixed capital investment

10) Amortization was for 20 years at 4% interest.

Cost estimates by this method will probably be lower than those which will be found in most industrial situations since relatively low carbon costs, carbon losses, and interest rates were assumed. Ford (1971) has estimated that costs near 25 cents per 1000 gallons are more typical.

Chemical Treatment

Chemical treatment costs for pesticide wastes cannot easily be quantified because of the widely differing waste characteristics, the large number of chemicals that can be used and the degree of treatment required. However, some data are available on neutralization since it is a common practice in many industries. Figure 29 shows actual costs for typical neutralization facilities for petrochemical wastes receiving lime treatment. Chemical costs for the plants surveyed in this study ranged from $0.50 per ton for waste lime sludge used by one chlorinated hydrocarbon manufacturer to $16.00 per ton for slaked lime used after limestone trench treatment of a similar chlorinated herbicide waste stream. Lime trench treatment can be performed at considerably less cost since large contact basins are not needed. Limestone costs varied from $0.50 per ton for low parity stone to $5.50 per ton for high quality stone.

Estimates of total chemical treatment costs for pesticide waste treatment at plants visited during this study include $400,000 per year for three stage chemical treatment of a 14 gpm organophosphorus waste stream. Eventually, thermal evaporation will also be employed at the organophosphorus plant increasing the costs somewhat. A second plant indicated that 25% of the capital cost of the facility was allocated to pollution control equipment.

Biological Treatment

Most published data on biological treatment processes deal with municipal sewage systems or industrial streams with similar characteristics. Figures 30-33 show typical costs that can be expected from various biological waste treatment unit processes. Table 24 contains a summary of generalized cost data for several treatment schemes used for industrial

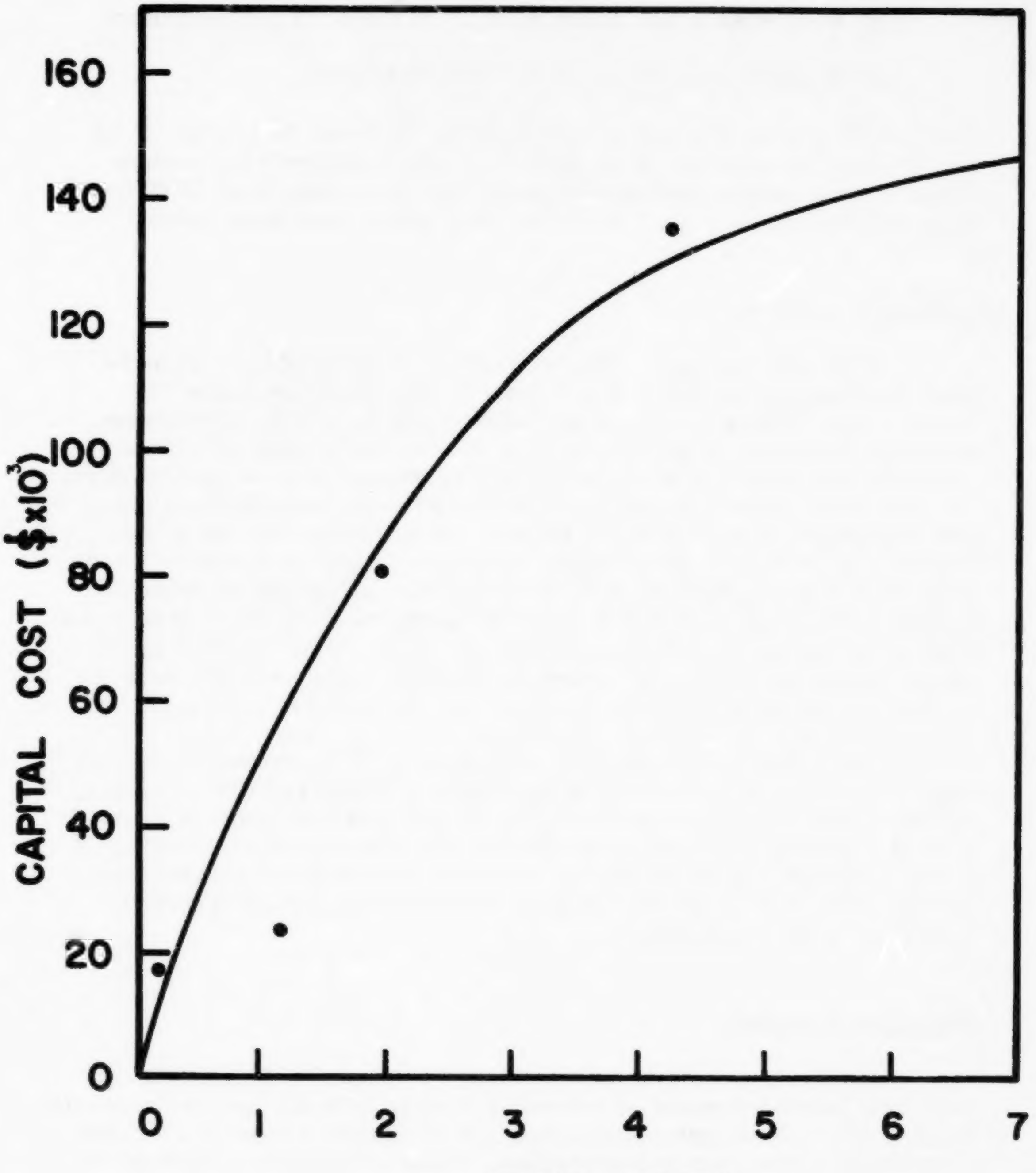

Figure 29. Capital Cost Relationship - Neutralization.

Source: Ford and Gloyna, 1970.

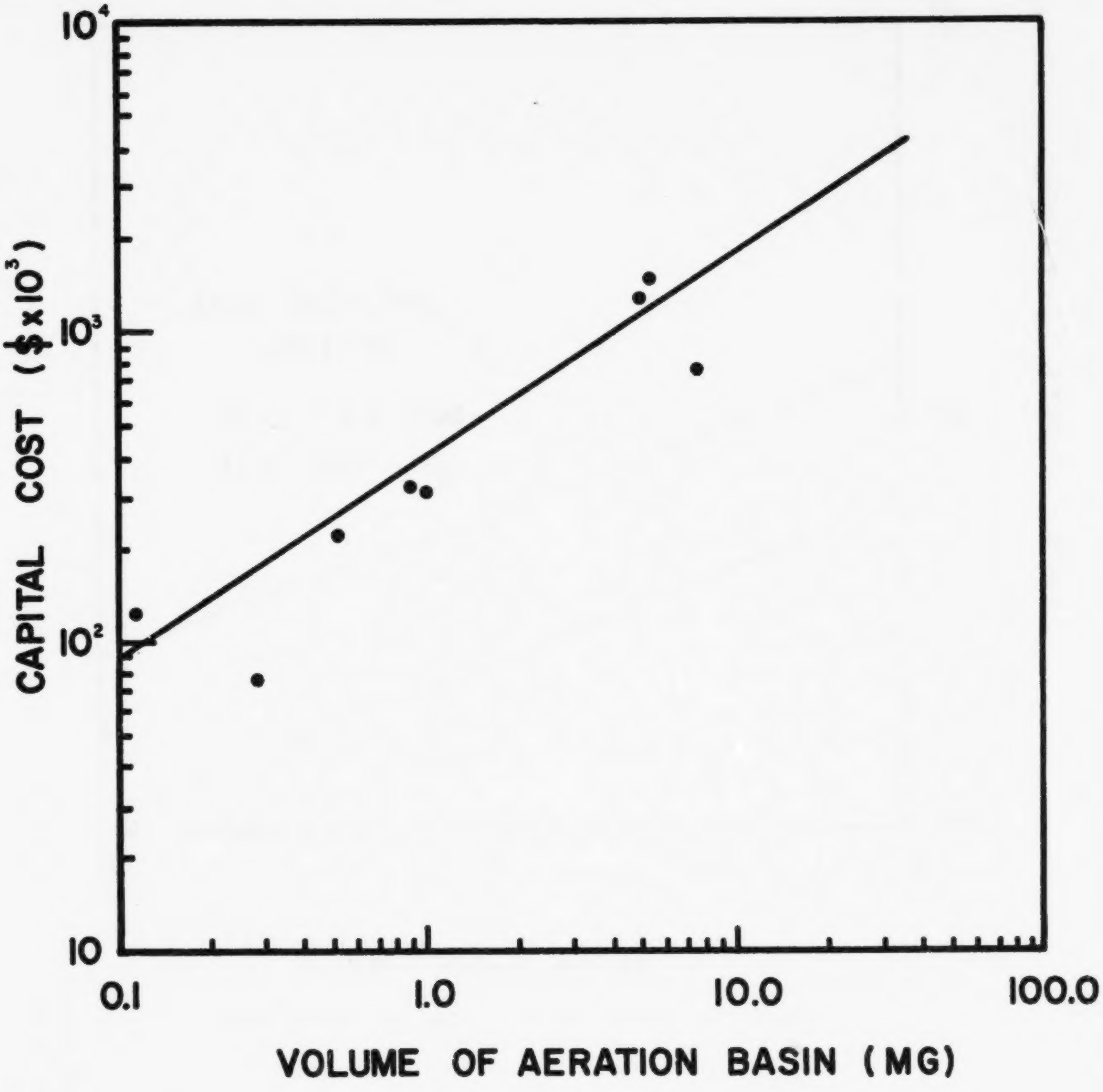

Figure 30. Capital Cost Relationship - Activated Sludge.

Source: Ford and Gloyna, 1970.

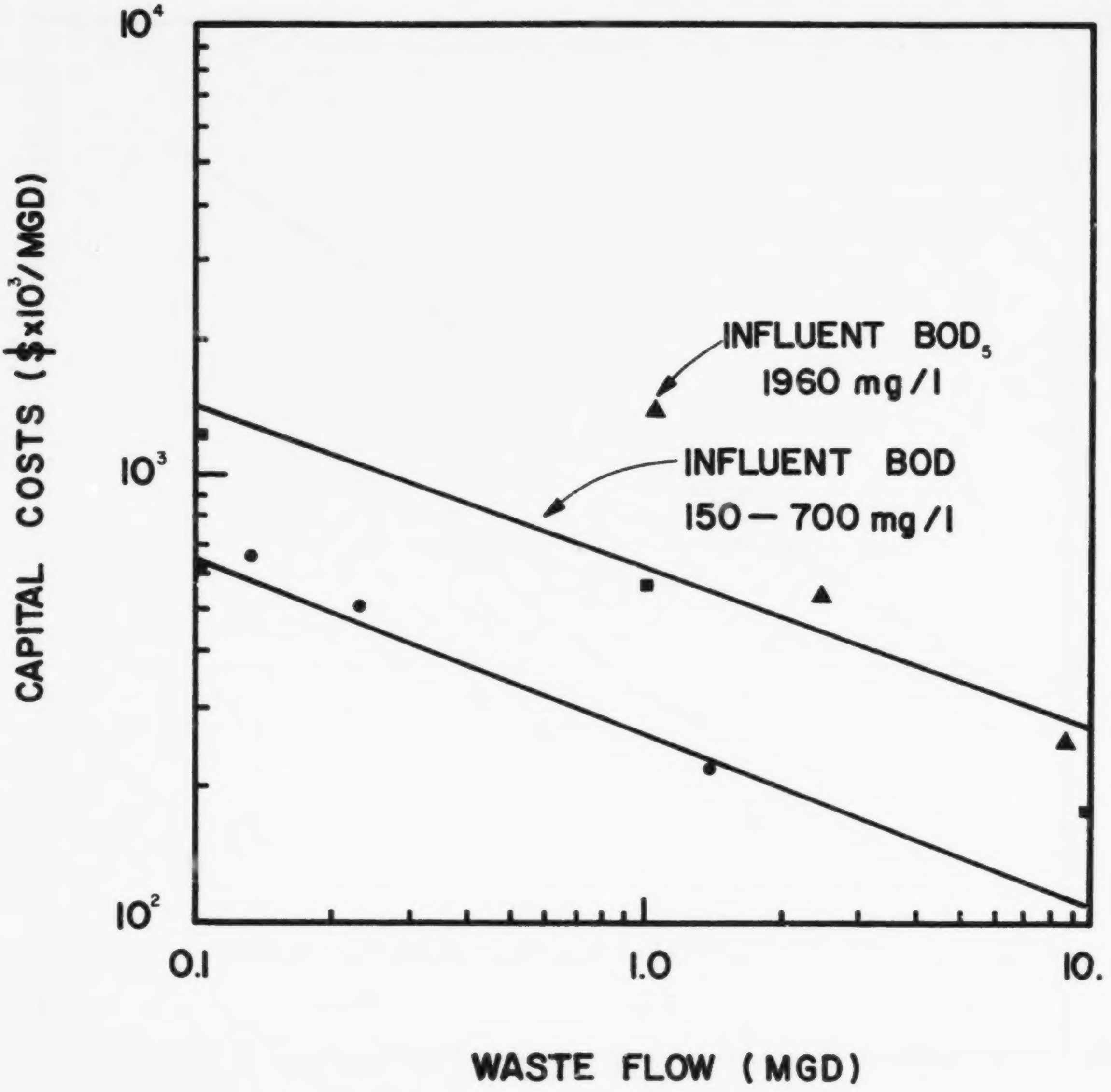

Figure 31. Capital Cost Relationship - Trickling Filters.

Source: EPA Report, 1970.

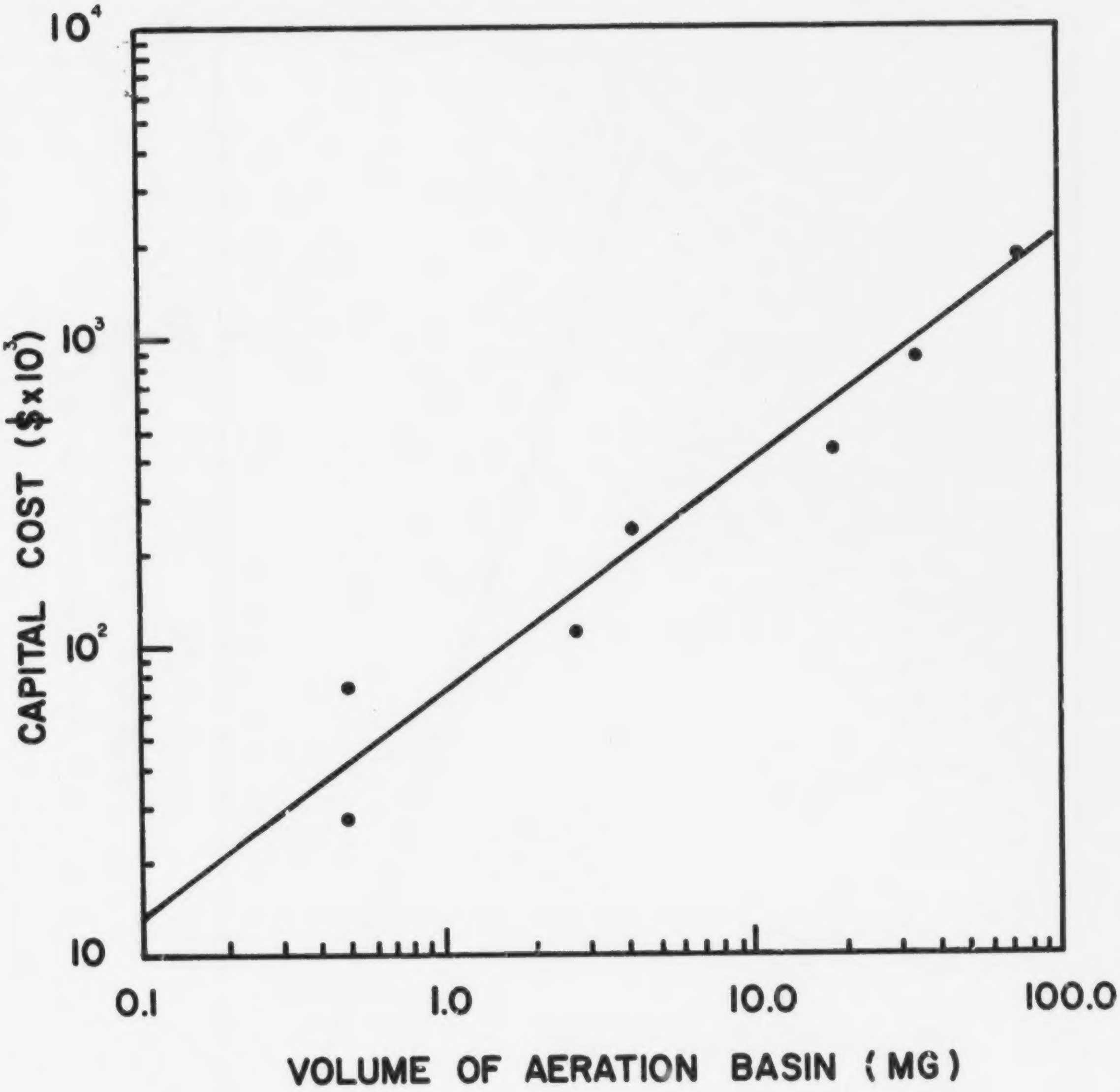

Figure 32. Capital Cost Relationship - Aerated Lagoon.

Source: EPA Report, 1970.

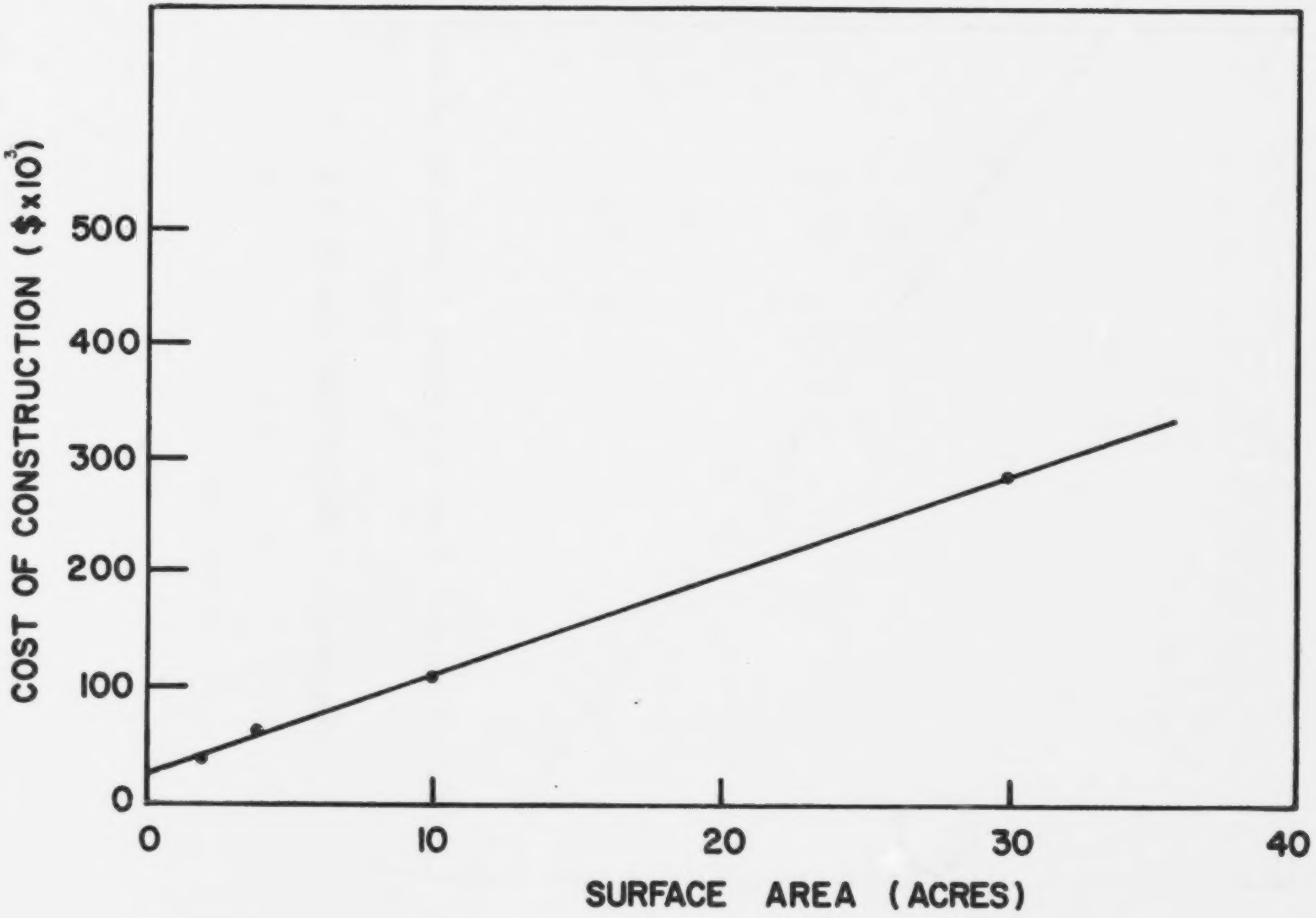

Figure 33. Capital Cost Relationship - Lagoons.

Source: EPA Report, 1970.

Table 24

COSTS FOR VARIOUS DEGREES OF TREATMENT FOR DIFFERENT COMBINATIONS OF WASTE CHARACTERISTICS

Waste BOD in mg/l

WASTE FLOW 1.0 MGD	3000		1000		500	
	Cost*	Effl. BOD	Cost*	Effl. BOD	Cost*	Effl. BOD
Pre or Primary	0.32	2700	0.32	900	0.32	450
Activated sludge	1.93	25	1.13	25	0.85	25
Sand filtration	2.40	15	1.61	15	1.05	15
Carbon adsorption	6.54	1	3.91	1	2.18	1
Ion exchange	7.17		4.54		2.18	
Anaerobic ponds	2.36	200	0.63	200	0.43	200
Aerated lagoon	1.61	100	0.51	100	0.58	100
WASTE FLOW 0.5 MGD						
Pre Primary	0.19	2700	0.19	900	0.19	450
Activated sludge	1.13	25	0.66	25	0.50	25
Sand filtration	1.42	15	1.00	15	0.81	15
Carbon adsorpt.	4.02	1	2.50	1	1.50	1
Ion exchange	4.36		2.83		1.84	
Anaerobic ponds	0.81	200	0.36	200	0.24	200
Aerated lagoons	0.97	100	0.51	100	0.35	100

*Costs are given as total capital costs in millions of dollars.
Source: Barnard, 1970.

wastes. From these data it can readily be seen that no single system can be considered the most economical for a variety of cases. Effluent requirements, flow volume, waste load, etc. must be considered. For example, as Table 24 shows, high flow, high BOD wastes may be treated more effectively and more cheaply with activated sludge than anaerobic ponds, but low flow, low BOD wastes are more cheaply (but less efficiently) treated with anaerobic ponds. In general, toxicity or pesticidal component removal will parallel BOD and COD reduction if the compound is biodegradable. Therefore, the same type of cost-effectiveness analysis used for industrial waste treatment should hold for pesticide wastes.

An alternate method of estimating the cost of waste water treatment is to determine the charges assessed by municipal treatment plants which accept industrial wastes. The idea of a city assessing surcharges on industry is gaining wide acceptance. However, pending legislation in the United States Congress will probably set pretreatment requirements for all industries discharging wastes into publicly owned treatment facilities which have received federal funds. These pretreatment requirements will have some effect on the present practice of industrial treatment in municipal plants, but until the legislation is approved in its final form, the magnitude of the effect cannot be estimated.

If the surcharge rates presently used are established to allow the the city to recover the added cost of treating the industrial waste , they should be indicative of treatment costs for large scale plants. Unfortunately, the rates established by municipalities can vary widely. Excessive charges are sometimes used to discourage industrial contributors that could overload a system, and conversely, low charges are sometimes set to encourage industries to use facilities that are experiencing financial difficulties. Therefore, examples of high average and low rates should be examined.

a) Low - Many large cities apply the same rates to any industrial discharge as they do domestic customers. Charges are usually set at some fixed percentage of water costs and range from \$0.03 to 0.12 per 1000 gallons. The cities normally require that the wastewater characteristics be determined and the discharge must be shown treatable prior to acceptance.

b) Average - A small municipality in a North Atlantic state with a 30 MGD plant, charges an organic chemical plant \$0.40 per 1000 gallons for flows up to 0.75 MGD. No surcharge based on organic loading or treatability is included.

c) High - A major North Atlantic city charges \$0.70/1000 gallons for flows less than 0.03 MGD and decreasing amounts to \$0.44/1000 gallons for flows exceeding 0.57 MGD.

Various schemes exist for sewage charge determinations in cities which feel that the additional cost incurred for testing, monitoring and reporting wastewater characteristics is worthwhile. The City of Philadelphia assesses a surcharge of \$0.15 per pound of BOD above 350 mg/l or suspended solids above 400 mg/l. Their studies show that it presently costs \$0.06/1000 gallons to provide primary and secondary treatment and from \$0.036 to \$0.04/1000 gallons to provide primary treatment only to mixed industrial and municipal wastes. (Water Dept.- City of Philadelphia, 1970). The City of Chicago charges industry unit prices of \$0.21 per 1000 gallons of flow plus \$0.014 per pound of BOD_5 plus \$0.024 per pound of suspended solids for large discharges (Malin, 1971). This system requires extensive self-monitoring and reporting from the industry plus a large amount of spot sampling conducted by the city crews.

The City of New York has developed an ordinance which allows an industrial surcharge, D, to be assessed, based on the formula:

$$D = C\,F\,V\left[(SS - 350) + (BOD - 300)\right]$$

where D = the amount of surcharge in dollars
C = actual cost per pound for removing pollutants
F = a conversion factor (mg/l to #/million gallons)
V = waste discharge volume in ft^3
SS = suspended solids concentration
BOD = Biochemical Oxygen Demand

The figures, 350 and 300, are the concentrations of suspended solids and BOD, respectively, below which there is no charge to industry. The cost factor C is recalculated each year and is currently set at \$0.025 per pound (Malin, 1971).

Incineration

Liquid, semi-solid and solid wastes from pesticide manufacturers are burned in several types of furnaces. The multiple-chamber spray injection furnace is the type most often used. Natural gas or fuel oil is used as auxiliary fuel to insure proper combustion. The total incineration costs are dependent on the capacity requirements, BTU value of the waste be to burned, operating temperature, waste injection method and gas cleaning requirements. Figure 34 summarizes a large amount of data on liquid waste incineration.

Vortex furnaces for high BTU liquid wastes and fluidized bed incinerators for solid wastes are being investigated by pesticide manufacturers. The total cost of these units is high because of increased maintenance and operating costs. Capital costs may be somewhat lower than more conventional units since the higher heat rates and heat transfer capabilities reduce the required size of the units for a given waste volume. Few vortex units are in operation to date so meaningful cost data are not available. However, European experience with fluidized bed units indicates that capital costs should range from $60 to $120 per pound per hour of capacity, and operating costs should be near $5.00 per ton for small units (1600 #/hr) to less than $1.00 per ton for 8000 pounds per hour and larger units (Witt, 1971).

A major cost factor that must be included in incinerator feasibility studies is the cost of the required air cleaning equipment. In order to meet present and proposed air control regulations (Ringelmann #1 plume opacity, SO_2 and particulates based on process weight, NO_x based on BTU rating) precipitators, filters (for particulates only) or flue gas scrubbers must be employed. The capital and operating costs for these devices can exceed the costs of small incinerator units and may represent as much as 25% of the total cost of very large installations. Water treatment requirements for the scrubber blowdowns also represent a significant cost factor. As a rule of thumb, for incinerator units with capacities greater than 1000 pounds per hour, adequate air cleaning (including blowdown treatment and solids handling) should cost a minimum of 25% of the incinerator costs. If unusually restrictive air cleaning is required because of acid mists, toxic aerosols, etc., this cost may increase.

Burial

The most widely used disposal method for wastes from pesticide manufacture is burial. Almost all plants visited used burial for the ultimate disposal of some portion of their waste. According to Heaning and Keane (1971) burial by landfill, including proper compaction and cover can be accomplished for approximately $1.50 per ton for large scale

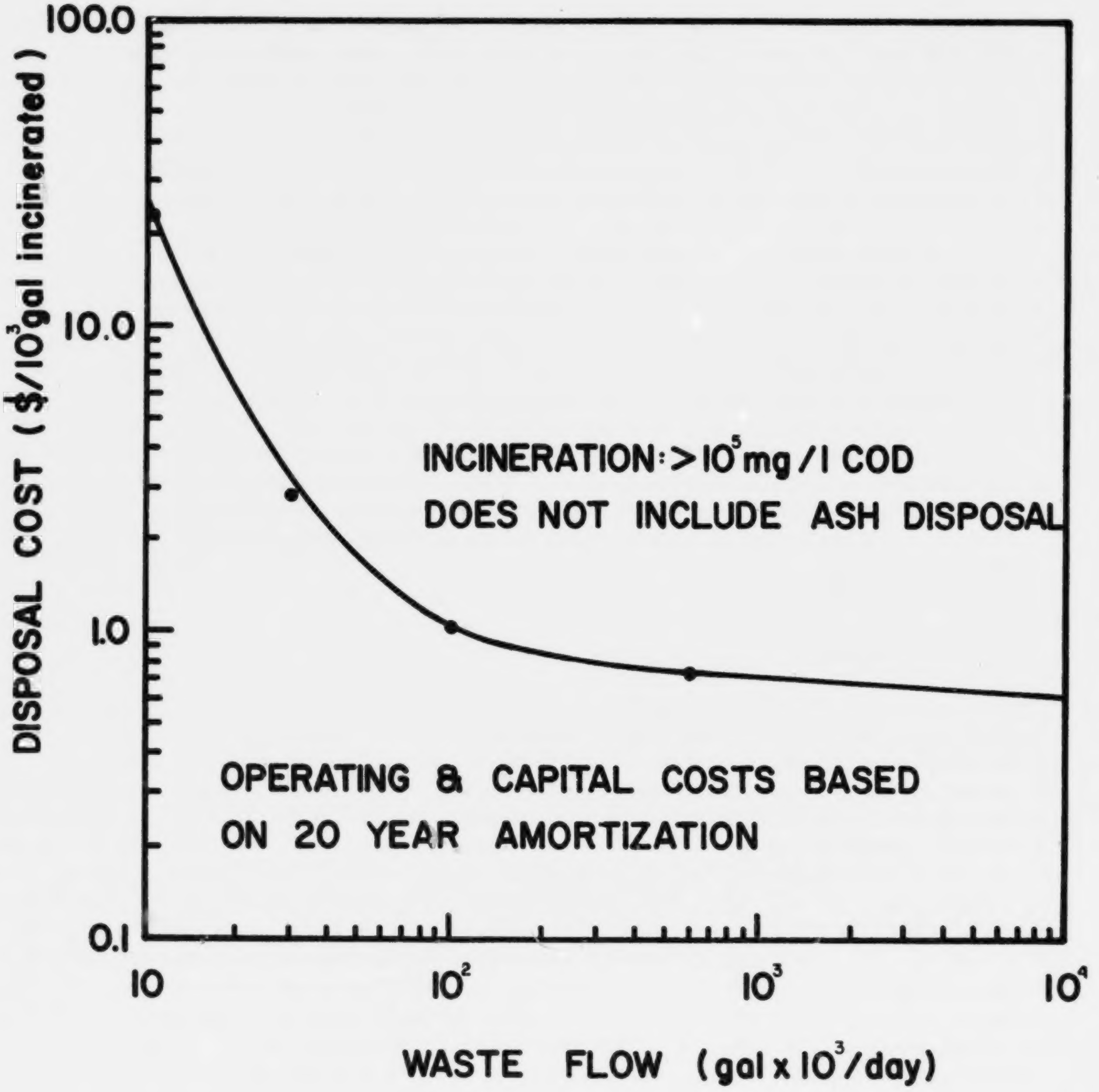

Figure 34. Capital Cost Relationship - Incineration.

Source: EPA Report, 1970.

operations (50,000 tons per year) or near $5.00 per ton for small fills (10,000 tons per year). This includes labor costs, equipment costs, and miscellaneous expenses such as road maintenance, landscaping and surveying. The data are summarized in Figure 35. There is no allowance for costs of land, site preparations, or haul in this figure. These data were obtained from studies of municipal waste disposal and should be generally applicable to landfilled pesticide manufacturing wastes.

Since pesticide wastes require special care in handling and hauling to reduce the possibility of the escape of toxic compounds, the cost of haul to the fill site may be significant. The wide variations in equipment requirement, labor costs, haul distances, topography and road conditions make it impossible to estimate the cost of haul. This information must be obtained for each specific set of circumstances.

Likewise, the cost of pit disposal, without interim cover or compaction, is highly variable and cannot be estimated for the "normal" case. In general this type of burial is much cheaper in the short term, but has a higher probability of causing future problems than the landfill method.

Ocean Disposal

In coastal areas ocean dumping is often a relatively low cost waste disposal method. However, new regulatory practices will undoubtedly make this method more costly, if not impossible. Table 25 contains estimates of the present cost of ocean disposal for various types of waste including industrial wastes. The figures indicate that bulk industrial wastes cost an average of $1.70 per ton in 1968 while containerized wastes averaged $24.00 per ton. Based on data from this report, the average cost for bulk industrial waste is approximately $2.00 per ton. If the waste flow is large enough to require a 5000 ton barge on a regular schedule, the costs per ton may be reduced to $0.50 per ton. Excessive haul distances (> 100 miles) and on-shore storage requirements increase the cost of this type of disposal. The wide range in costs for containerized industrial wastes (Table 25) reflects the difference between long-term contractual operations and the causal disposal of small amounts of toxic and hazardous wastes by a single producer (Witt, 1971). For example, the disposal of one lot of 500 barrels containing 115 tons of liquid waste requires the one time use of a barge and tug. Depending on the geographical area and the location of the disposal site, the approximate cost would be over $2000, or $17 per ton.

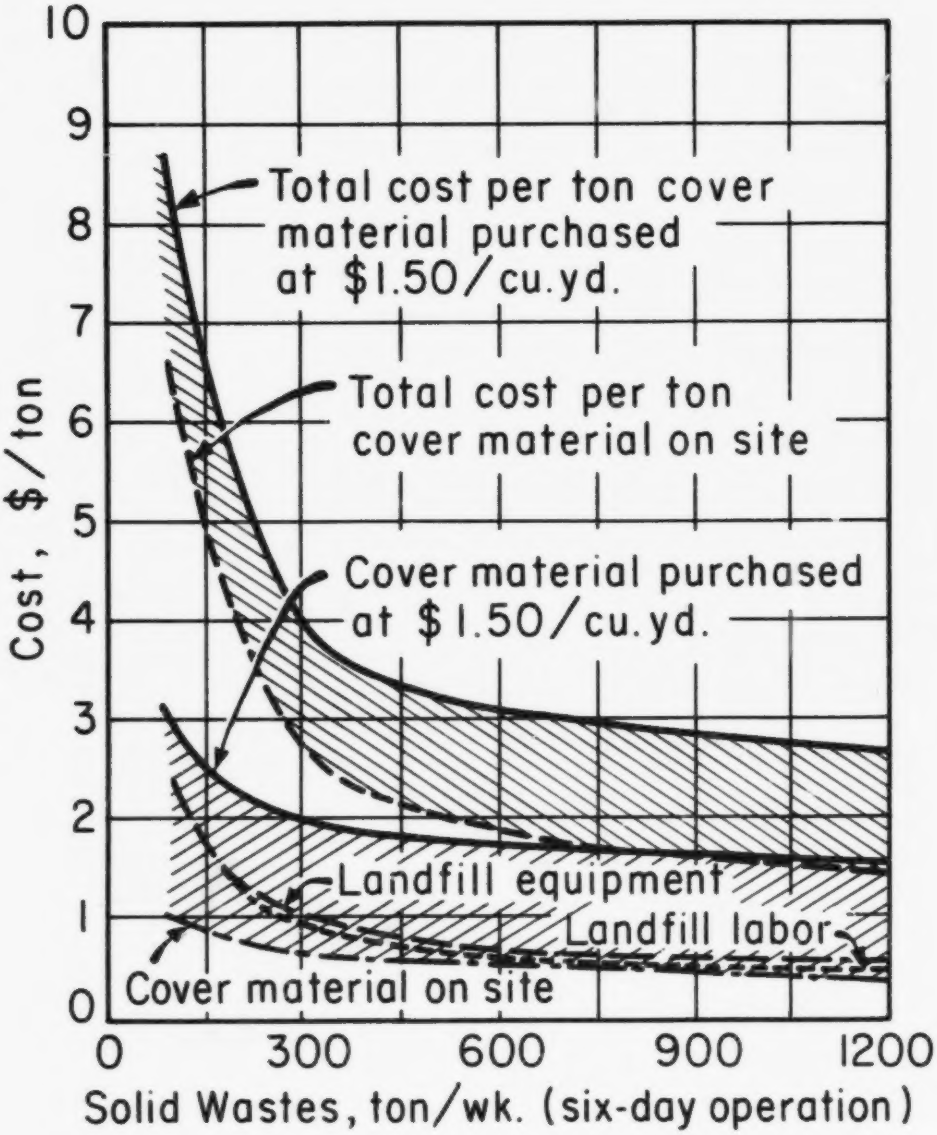

Figure 35. The Cost of Solid Waste Disposal in Sanitary Landfills.

Source: Heaney, et al., 1970.

Table 25

Estimated Marine-Disposal Cost for 1968

	Pacific Coast		Atlantic Coast		Gulf Coast		Total	
Type of Waste	Annual Tonnage	Estimated Cost, $	Annual Tonnage	Estimated Cost, $	Annual Tonnage	Estimated Cost, $	Annual Tonnage	Estimated Cost, $
Dredging spoils	7,320,000	3,175,000	15,808,000a	8,608,000	15,300,000	3,800,000	38,428,000	15,583,000
Industrial wastes	981,000	991,000	3,011,000	5,406,000	690,000	1,592,000	4,682,000	7,989,000
containerized	300	16,000	2,200	17,000	6,000	171,000	8,500	204,000
Refuse [b]	26,000	392,000					26,000	392,000
Sludge [c]			4,477,000	4,433,000			4,477,000	4,433,000
Miscellaneous	200	3,000					200	3,000
Construction & demolition debris			574,000	430,000			574,000	430,000
Explosives			15,200	235,000			15,200	235,000
Total wastes [d]	8,327,500	4,577,000	23,887,400	19,129,000	15,986,000	5,563,000	48,210,090	29,269,000

[a] Includes 200,000 tons of fly ash.

[b] At San Diego, 4,700 tons of vessel garbage at $280,000 dumped in 1968 (discontinued in Nov. 1968).

[c] Tonnage on wet basis. Assuming average 4.5% dry solids, this amounts to about 200,000 tons/yr. of dry solids being barged to sea.

[d] Radioactive wastes omitted because sea-disposal operations were terminated in 1967.

Source: (Witt, 1971).

CHAPTER XIII

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CHAPTER IX

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CHAPTER X

APPENDICES

Page No.

A. Common and Chemical Name, Oral Toxicity, Solubility, and Soil Persistence of Some (Representative) Important Pesticides 158

B. Injection Well Act, State of Texas, Article 762b, V.T.C.S. as Amended by 61st Legislature, Regular Session, 1969 165

C. Proposed Regulations, State of California, Subchapter 15, Waste Disposal to Land 169

D. Statement by Governor William T. Cahill of New Jersey on Sludge Barging to Sea, February 15, 1970 177

APPENDIX A

I. Common and chemical name, oral toxicity, solubility, and soil persistence of some (representative) important pesticides.

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in soil **
Chlorinated Hydrocarbon Insecticides				
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8 8a, hexahydro-1,4-endro-exo-5,8-dimethanonaphthalene	55	27 ppb	3
BHC	benzenehexachloride	500-6000	insol.	3
Chlordane	octachloro-4,7-methanotetrahydroindane	570	insol.	3
DDD	1,1-dichloro-2,2-bis (p-chlorophenyl) ethane	2500-3400	insol.	3
DDT	1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane	113	insol.	3
Dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene	60	185 ppb	3

** 1 = 1 to 3 months; 2 = 3 to 12 months; 3 = more than 12 months

Source: Working Group on Pesticides, 1970.

APPENDIX A I. (Continued)

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in Soil
Endosulfan	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-Benzodioxathiepin-3-oxide	110	insol.	3
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene	7.3 - 43.4	insol.	3
Heptachlor	1,4,5,6,7,8,8a-haptachloro-3a,4,7a-methanoindene	130 - 135	56 ppb	-
Lindane	1,2,3,4,5,6-hexachlorocyclohexane	90	insol.	3
Methoxychlor	2,2-bis (p-methoxypheyl)-1,1,1-trichloromethane	6000	insol.	-
Strobane	terpene polychlorinates	220	insol.	3
Toxaphene	chlorinated camphene	90	insol.	-
Organophosphorous Insecticides				
Carbonphenothion	S- (p-chlorophenylthio) methyl O,O-dicthyl phosphorodithioate	32.2	2 ppm	

APPENDIX A I. (Continued)

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in soil
Demeton	O-[2-(ethylthio) ethyl] phosphorothioate (thiono isomer) I and O, O-diethyl-S-[2-(ethylthio) ethyl] phosphorothioate (thiolisomer) II	2.5 - 12	60 ppm	1
Diazinon	O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate	76 - 108	40 ppm	2
Dichlorvos	2,2-dichlorovinyl dimethyl phosphate	56 - 90	1000 ppm	-
Dimethoate	0,0-dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate	185-245	7000 ppm	-
Ethion	O,O,O',O'-tetraethyl S,S'-methylene biophosphorodithioate	208	insol.	-
EPN	O-ethyl-O-p-nitrophenyl phenylphosphorothioate	14 - 42	insol.	-
Malathion	O,O-dimethyl phosphorodithiate of diethyl mercaptosuccinate	2800	145 ppm	1
Methyl-parathion	O,O-dimethyl O-p-nitrophenyl phosphorothioate	9.4	50 ppm	1

APPENDIX A I. (Continued)

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in soil
Mevinphos	2-carbomethoxy-1-methylvinyl dimethyl phosphate, isomer	6 - 7		1
Parathion	O,O-diethyl O-p-nitrophenyl phosphorothioate	6 - 15	24 ppm	1
Phorate	O,O-diethyl S-(ethylthio)-methyl phosphorodithioate	1.6 - 3.7	85 ppm	1
Ronnel	O,O-dimethyl-O-(2,4,5-trichlorophenyl) phosphorothioate	1.75	40 ppm	1
Methyl Carbamate Insecticides				
Carbaryl	N-methyl-1-naphthylcarbamate	540	< 0.1%	1
Mobam	4-benzothienyl-N-methylcarbamate	234	-	-
Zectran	4-dimethylamino-3,5-xylyl methylcarbamate	15	-	-
Mesurol	4-(methylthio)-3,5-xylylmethylcarbamate	130	-	-

APPENDIX A I (Continued)

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in soil
Baygon	2-iso-propoxy-phenol-N-methylvarbamate	100	-	-
Temik	2-methyl-2-(methylthio) propionaldehyde O-(methylcarbamoyl) oxime	0.93	-	-
Isolan	1-isopropyl-3-methyl-5-pyrazoly-dimethyl carbamate	11	-	-
Phenoxyalkanoic Acid Herbicides		mg/kg	ppm	
2,4,D	2,4-dichlorophenoxyacetic acid	300 - 1000	620	1
2,4,5-T	2,4,5-trichlorophenoxyacetic acid	100 - 300	251	2
MCPA	2-methyl-4-chlorophenoxyacetic acid	700	825	1
s-Triazine Herbicides				
Simazine	2-chloro-4,6-bis (ethylamino)-s-triazine	>5000	5	2
Atrazine	2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine	1750 - 3080	33	3

APPENDIX A I. (Continued)

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in soil
Prometryne	2-methylthio-4,6-bis (isopropylamino)-	3750	48	1
Substituted Urea Herbicides				
Monuron	3-(p-chlorophenyl)-1,1-dimethylurea	3600	230	2
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	440	42	3
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	1500	75	2
Phenylcarbamate Herbicides				
CIPC	isopropyl-N-3-chlorophenylcarbamate	5000 - 7500	88	1
IPC	isopropyl-N-phenylcarbamate	5000	250	1
Thiolcarbamate Herbicides				
EPTC	S-ethyl N, n-dipropylthiolcarbamate	1630 (rat) 3160 (mice)	375	1
Pebulate	S-propyl butylethylthiocarbamate	1120	92	1

APPENDIX A I. (Continued)

Common Name	Chemical Name	Oral Toxicity LD_{50} (mg/kg)	Solubility in H_2O	Persistence in soil
Chlorinated Aliphatic Acids				
Dalapon	2,2-dichloropropionate	8000	90%	1
TCA	trichloroacetate	5000	54%	1
Amine Herbicides				
Trifluralin	α,α α -trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine	>10,000	<1	2

APPENDIX B

INJECTION WELL ACT
STATE OF TEXAS

Article 7621b, V.T.C.S.
as amended by 61st Legislature,
Regular Session, 1969

Section 1. SHORT TITLE. This Act may be cited as the Injection Well Act.

Section 2. DEFINITIONS. As used in this Act, unless the context requires a different definition:

(a) "board" means the Texas Water Quality Board;

(b) "commission" means the Texas Railroad Commission;

(c) "Person" means individual, corporation, organization, government or governmental subdivision or agency, business trust, partnership, associatiation, or any other legal entity;

(d) "Pollution" means the alteration of the physical, chemical, or biological quality of, or the contamination of, water that renders the water harmful, detrimental, or injurious to humans, animal life, vegetation or property, or to public health, safety, or welfare, or impairs the usefulness or the public enjoyment of the water for any lawful or reasonable purpose;

(e) "Industrial and municipal waste" is any liquid, gaseous, solid or other waste substance or a combination thereof resulting from any process of industry, manufacturing, trade, or business or from the development or recovery of any natural resources, or resulting from the disposal of sewage, or other wastes of cities, towns, villages, communities, water districts and other municipal corporations, which may cause or might reasonably be expected to cause pollution of fresh water;

(f) "fresh waters" means waters whose bacteriological, physical and chemical properties are such that they are suitable and feasible for beneficial use for the purposes permitted by law;

(g) "casing" means any material utilized to seal off strata at and below the earth's surface;

(h) "injection well" means an artificial excavation or opening into the ground, made by means of digging, boring, drilling, jetting, driving or otherwise, and made for the purpose of injecting, transmitting, or disposing of industrial and municipal waste into a subsurface stratum; also a well initially drilled for the purpose of producing oil and gas when used for the purpose of transmitting, injecting, or disposing of industrial and municipal waste into a subsurface stratum; but "injection well" does not include any surface pit, excavation or natural depression used to dispose of industrial and municipal waste.

(i) Notwithstanding any provisions of Subsection (e) of this section, "waste arising out of or incidental to the drilling for or the producing of oil or gas" includes, but is not limited to, the following items when they result from such drilling or producing activities; salt water, brine, sludge, drilling mud, and other liquid or semi-liquid waste materials.

Section 3. INDUSTRIAL AND MUNICIPAL WASTES; APPLICATIONS TO BOARD.

(a) Before any person commences the drilling of an injection well, or before any person converts any existing well into an injection well, for the purpose of disposing of industrial and municipal waste, other than waste arising out of or incidental to the drilling for or the producing of oil or gas, a permit therefore shall be obtained from the board. The board shall be available upon request without cost. The board shall require the furnishing of such information by an applicant as the board may deem necessary to discharge properly the duties imposed by this Act. An application for a permit to drill an injection well, or to convert any existing well to an injection well, shall be accompanied by a fee of $25.00 which shall be collected by the board for the benefit of the state.

(b) Upon receipt by the board of an application in proper form and accompanied by the necessary fee for a permit to drill an injection well, or to convert an existing well to an injection well, the board shall cause an inspection to be made of the location of the proposed injection well to determine local conditions and the probable effect of the injection well, and shall cause an evaluation to be made to determine the requirements for the setting of casing, as provided in Section 5 of this Act.

(c) The board shall also send copies of every application received in proper form to the Texas Water Development Board, the Texas State Department of Health, the Texas Water Well Drillers Board, and to such other persons as the board may designate. The agencies and other persons to whom a copy of the application is sent may make recommendations to the board concerning any aspect of the application, and shall have such reasonable time to do so as the board may prescribe.

(d) The board may hold a public hearing upon an application if it is deemed necessary and in the public interest, but otherwise, a public hearing is not required. Notice of any public hearing and its procedure shall be under such terms and conditions as the board may prescribe.

(e) Any person applying to the board for a permit to inject industrial and municipal waste, other than waste arising out of or incidental to the drilling for or the producing of oil or gas, into a subsurface stratum shall submit with the application a letter from the commission stating that the drilling of the injection well and the injection of industrial and municipal waste into the subsurface stratum will not endanger or injure any oil or gas formation.

Section 4. ISSUANCE OF PERMIT; CASING OF WELL; RULES AND REGULATIONS.

If the board or commission, as the case may be, finds that the installation of the injection well is in the public interest, will not impair any existing rights, and that by requiring proper safeguards both ground and surface fresh waters can be protected adequately from pollution, the board or commission, as appropriate, may grant the application in whole or in part and issue a permit with such terms, provisions, conditions and requirements as are reasonably necessary to protect fresh waters from pollution by industrial and municipal waste. Specifically, the board or commission shall require that the injection well shall be so cased as to protect all fresh waters from pollution by the intrusion of industrial and municipal waste. The casing shall be set at such depth, with such materials, and in such manner as the board or the commission may require. The board or the commission, in establishing the depth to which casing shall be installed, shall consider known geological and hydrological conditions and relationships, the foreseeable future economic development in the area, and the foreseeable future demand for the use of the fresh waters in the locality. The board or commission may also require the permittee to keep and furnish a complete and accurage record of the depth, thickness and character of the different strata penetrated in the drilling of the well. In the event an existing well is to be converted to an injection well, the board or commission may require that the applicant furnish an electric log or a drilling log of the existing well. A copy of every permit issued by the board shall be furnished by the board to the commission, the Texas Water Development Board, the Texas State Department of Health, and the Texas Water Well Drillers Board. A copy of every permit issued by the commission shall be furnished by the commission to the board, which shall in turn forward copies to the other agencies named in the preceding sentence. The board and the commission each shall adopt rules, regulations and procedures reasonably required for the performance of the duties, powers and functions prescribed for each by this Act. Copies of any rules or regulations under this Act proposed by the board or the commission shall, before their adoption, be sent by each of these agencies to the other agency, and also to the

Texas Water Development Board, the State Department of Health, the Texas Water Well Drillers Board, and such other persons as the originating agency may designate. Any agency or person to whom the copies of proposed rules and regulations are sent may submit comments and recommendations to the agency proposing the rules and regulations, and shall have such reasonable time to do so as the originating agency may prescribe.

Section 5. WILLING COPY OF PERMIT. Any person receiving a permit to inject industrial and municipal waste, shall, before injection operations are begun, file a copy of the permit with the health authorities of the county, city and town where the well is located.

Section 6. ENFORCEMENT. Any person who fails to comply with the provisions of this Act, or with any rule or regulations promulgated by the board or the commission under this Act, or with any term, condition or provision in his permit issued pursuant to this Act, shall be subject to a civil penalty in any sum not exceeding One Thousand Dollars ($1,000.00) for each day of non-compliance and for each act of non-compliance, as the court may deem proper. The action may be brought by the board or the commission, as appropriate, in any court of competent jurisdiction in the county where the offending activity is occurring or where the defendant resides. Full authority is also given the board or commission, as appropriate, to enforce by jurisdiction in the county where the offending activity is occurring, any and all reasonable rules and regulations promulgated by it which do not conflict with any law, and all of the terms, conditions and provisions of permits issued by the board or commission pursuant to the provisions of this Act. At the request of the board or the commission, the attorney general shall institute and conduct a suit in the name of the State of Texas for injunctive relief or to recover the civil penalty, or for both the injunctive relief and civil penalty, authorized in this section. Any party to a suit may appeal from a final judgment as in other civil cases. The obtaining of a permit under the provisions of this Act by a person shall not act to relieve that person from liability under any statutory law or the Common Law.

APPENDIX C

PROPOSED REGULATIONS
STATE OF CALIFORNIA

Subchapter 15
Waste Disposal to Land

Article I
General Provisions

Section 2500 DEFINITION OF TERMS. (a) "Disposal site" means any place used for the disposal of solid or liquid wastes. It does not include sewage treatment ponds or locations of waste disposal from pipes or ditches into waters of the state.

(b) "Disposal Area" is the actual area of the site which has received or is receiving wastes.

(c) "Percolate" is fluid resulting from the percolation or draining of a liquid through a waste substance.

(d) "Usable" ground or surface water includes potentially usable water.

(e) "Hydraulic continuity" is a condition existing when fluid occupying an interstice of a saturated material is able to move, under a head differential imposed by gravity, to adjoining interstices and/or surface channels containing fluid.

(f) "Capillary fringe" is the partly saturated zone immediately above the water table in which water is held by capillary forces.

Section 2501. DISPOSAL AT CLASSIFIED SITES. Disposal of either solid or liquid wastes at disposal sites shall be only at those sites which have been classified by the appropriate regional water quality control board in the establishment of waste discharge requirements in conformity with this subchapter unless requirements are waived by the regional board pursuant to Section 2530 (c).

Article 2
Classification of Waste Disposal Sites

Section 2510. CLASS I DISPOSAL SITES. Class I disposal sites are those at which protection is provided for the quality of ground and surface waters from all wastes as determined by the following criteria:

(a) The disposal area is underlain by non-waterbearing geological formations or by unusable groundwater which is isolated from other usable waters.

(b) Geological conditions must be naturally capable of preventing both vertical and lateral continuity between liquids and gases from waste in the site and usable groundwaters, or have been modified to achieve such capability in a manner acceptable to the regional board.

(c) Underlying geological formations which contain rock fractures or fissures of questionable permeability must be sealed to provide a competent barrier to the movement of liquids or gases from the disposal site.

(d) Surface drainage from tributary areas outside the site must be precluded from entering areas of the site which have received or are receiving wastes until the site is closed in accordance with requirements of the regional board.

(e) Subsurface flow into the disposal area and percolate resulting from internal drainage shall be contained within the site unless other disposition is made in accordance with requirements of the regional board.

(f) Class I sites made suitable for use by man-made physical barriers shall not be located where improper operation or maintenance of man-made physical containment structures will impair usable ground or surface water quality or create a hazard to public health.

(g) Class I sites shall not be located over zones of active faulting or where other forms of geological change would reduce the capability of natural or man-made features to prevent continuity with usable groundwaters.

(h) Class I sites for unlimited use must not be subject to washout or inundation by floods.

(i) Sites which comply with a,b,c,e,f, and g but would be subject to inundation by a flood of greater than 100 year frequency may be classified by the regional board as a limited Class I Disposal Site subject to waste discharge requirements which would include limits on (1) the type and quantity of material entering the site, (2) the concentration of material in the waste deposited on the site, (3) the amount of residue present or remaining on the site after evaporation of the liquid.

Section 2511 CLASS II DISPOSAL SITES. Class II disposal sites are those at which protection is provided to water quality from Group 2 and Group 3 wastes as determined by the following criteria:

(a) If the site has hydraulic continuity with usable ground or surface water, there must be physical features to prevent degradation of groundwater quality due to liquid or gases emanating from the waste. The types of physical features and the extent of protection of groundwater quality further divides Class II sites into two general categories.

(1) A Class II-1 site is isolated from vertical hydraulic continuity with usable groundwater by natural impervious geological formations or artificial barriers, or it is underlain by non-waterbearing rocks, but it may have lateral hydraulic continuity with groundwater basins containing usable groundwater.

(2) A Class II-2 site may have vertical hydraulic continuity with usable groundwater but it is either modified by artificial barriers or has natural geological and hydraulic features, such as soil type and depth to groundwater, which prevent degradation of the quality of usable groundwater underneath the site.

(b) Class II disposal sites located in flood plains shall be protected by natural or artificial features so as to assure protection from washout and flooding which could occur as a result of floods having a predicted frequency of once in 100 years.

(c) Surface drainage from tributary areas shall be precluded from contacting waste in the site.

(d) Gases emanating from waste in the site will be prevented from degrading groundwater during the predictable life of the site by physical features or rate of groundwater movement in hydraulic continuity with the site.

(e) Internal drainage of the site or subsurface flow into the site and the depth at which water soluble materials are placed shall be controlled during construction and operation of the site to minimize percolate and assure that the waste material will be above the highest anticipated elevation of the capillary fringe of the groundwater. Such control may include discharge from the site subject to waste discharge requirements prescribed by the regional board.

Section 2512 CLASS III DISPOSAL SITES. Class III disposal sites are those at which protection is provided for water quality from Group 3 wastes as determined by the following criteria:

(a) Each site is located and constructed to prevent erosion or transport of deposited material.

(b) Operation or construction of the site shall not result in degradation of surface water quality due to erosion of adjacent land areas.

Section 2513 WASTE WELLS. Wells suitable for the disposal of wastes shall provide protection to usable groundwater from wastes of Groups 1 or 2 in any form as determined by the following conditions:

(a) The receiving formation shall not be in hydraulic continuity with any usable groundwater.

(b) The construction and injection procedure will be such that no paths of percolation are developed which will permit the movement of the waste to a usable aquifer or to the surface.

(c) Certification has been provided by the California Division of Oil and Gas that construction and operation of waste wells under its jurisdiction will conform to regulations of the Division.

(d) Wells used for the disposal of wastewater and the resultant recharge of groundwater, or for the disposal of used irrigation water, under requirements adopted by the regional board may be exempted from provisions a, b, and c.

(e) Construction and operation of sewer wells shall be in conformance with applicable regulations for the protection of public health.

Article 3
Classification of Wastes Discharged to Land

Section 2520 GROUP I WASTES. Group I wastes consist of or contain substances directly harmful or dangerous to the health and safety of man or other living organisms during disposal operations or in the event of mixing with usable water, or substances which may significantly impair the quality of usable waters. Examples include but are not limited to the following:

(a) Municipal Wastes
    (1) Saline fluids from water or waste treatment and reclamation processes.
    (2) Community incinerator ashes.
(b) Industrial Wastes
    (1) Saline brine from food processing, oil well production, water treatment, industrial processes and geothermal plants.
    (2) Toxic or hazardous fluids from industrial processes or resulting from spills, or blowdown. These fluids may include spent cleaning fluids, petroleum fractions, chemicals, acids, alkalies, phenols, and spent washing fluids.

- (3) Substances from which toxic materials can leach such as process ashes, chemical mixtures, and mine tailings.

(c) Agricultural Wastes

- (1) Agricultural chemicals such as herbicides, insecticides, fungicides, and chemical fertilizer and their containers to the extent they are actually toxic or hazardous to human health or water quality after mixing with water.

(d) Other toxic wastes such as compounds of arsenic or mercury, chemical warfare agents, etc.

Section 2521 GROUP 2 WASTES. Group 2 wastes consist of or contain decomposable organic material which does not include substances which are toxic or significantly impair the quality of usable water. Group 2 wastes may be deposited in either a Class II-1 or II-2 site unless specifically limited by the regional board or the regulations of other appropriate authorities. Examples include but are not limited to the following:

(a) Municipal and industrial wastes

- (1) Garbage consisting of putrescible wastes from processing, preparation, cooking, and serving of food
- (2) Market wastes from handling, storage, and processing of produce
- (3) Construction and demolition materials containing paper, cardboard, tin cans, wood, glass, bedding, rubber products, roofing paper, wallpaper, stumps, and other materials
- (4) Rubbish and street refuse consisting of putrescible and non-putrescible material such as sweepings, dirt, leaves, catch basin dirt, litter, yard clippings, glass, paper, wood and metals in various forms or combinations.
- (5) Dead animals
- (6) Abandoned vehicles
- (7) Sewage treatment residue including solids from screens and grit chambers and sludge
- (8) Water treatment residue including solid organic matter collected on screens and in settling tanks
- (9) Ashes from household burning

(10) Infectious materials and hospital or laboratory wastes authorized for disposal to land by official agencies charged with control of plant, animal, or human disease.

(11) Magnesium and other highly flammable or pyrophoric materials

(12) Miscellaneous industrial wastes such as metals and metal products, wood and paper materials, oils, chemicals and sludges which are not toxic or hazardous within the definition of Group 1 wastes.

(b) Agricultural wastes

(1) Stalks, vines, green drops, culls, stubble, hulls, lint and seed from field and seed crops

(2) Vines, stalks, roots, green drops, and culls from vegetable crops

(3) Stumps, prunings and trimmings, culls, and green drops from fruit and nut crops

(4) Manures

(5) Dead animals or materials of animal origin.

Section 2523 DISPOSAL OF GROUP I WASTES IN CLASS II - I SITES.

Regional board may allow the disposal of certain Group I wastes in a Class II-1 site when, in the judgment of the board, such disposal will not constitute a threat to water quality. Such selected disposal of specific Group I wastes shall be subject to terms and conditions considered appropriate by the regional board.

Article 4
Implementation

Section 2530 WASTE DISCHARGE REQUIREMENTS FOR WASTE DISPOSAL SITES.

(a) Operators of existing sites for which requirements have not been prescribed, shall notify the appropriate regional board prior to July 1, 1972 for the purpose of receiving site classification and waste discharge requirements consistent with the provisions of this subchapter.

(b) Persons planning to establish new waste disposal sites or expand existing sites shall notify the appropriate regional board for the purpose of receiving waste discharge requirements prior to the disposal of waste at the new or expanded site in accordance with Section 13260 et seq of the Water Code.

(c) The regional board may waive the approval and classification of sites or the establishment of waste discharge requirements as provided by Section 13269 of the Water Code when an operation is not hazardous to water quality because of the type of waste and disposal operation, or an operation is in compliance with ordinances or regulations of other governmental agencies which adequately protect water quality. Such waivers shall be conditional and may be terminated by the regional board at any time.

(d) The disposal of wastes in a site prior to the installation and operability of physical structures and control measures required for compliance with waste discharge requirements is prohibited.

(e) Actions of the operator which impair or threaten to impair the physical integrity of the site may result in reclassification of the site or abatement proceedings by the regional board.

(f) Operators of Class I and Class II-1 sites shall be required to maintain records of the volume and type of Group I waste received at the site and the manner and location of disposal. Such records shall be maintained in good legible condition for a period of not less than ten years on forms provided by the board and in accordance with instructions which accompany the forms. Records shall be subject to inspection by representatives of the state or regional board at any time during normal business hours.

(g) Nothing in this subchapter shall be construed to limit the power of a regional board, city, county, or other jurisdiction to adopt and enforce equal or higher standards for the protection of water quality in connection with the disposal of waste materials to land, or to adopt and enforce land use restrictions which govern the location and operation of waste disposal sites.

Section 2531 COMPLETION OF FILL OPERATIONS.

(a) Prior to cessation of fill operations at a waste disposal site, the operator shall submit a technical report to the appropriate regional board describing the methods and controls to be used to assure protection of the quality of surface and groundwaters of the area during final operations and with any proposed subsequent use of the land. This report shall be prepared by or under the supervision of a registered and certified engineering geologist.

(b) The methods used to close a site and maintain protection of the quality of surface and groundwater shall comply with waste discharge requirements established by the regional board.

Section 2532 ABANDONMENT OF WASTE WELLS.

(a) Prior to abandonment of waste wells, the operator shall file a technical report with the appropriate regional board describing the methods and controls to be used for closing the well.

(b) Abandonment of waste wells, other than those within the jurisdiction of the Division of Oil and Gas, shall be under the supervision of a registered engineering geologist, a registered petroleum engineer, or the California Division of Oil and Gas.

(c) Abandonment of Wells within the jurisdiction of the Division of Oil and Gas shall be under the supervision and direction of the division.

APPENDIX D

Statement by Governor William T. Cahill of New Jersey on Sludge Barging to Sea

February 15, 1970

Earlier this week, it became necessary for me to proclaim a state of emergency in New Jersey in order to prevent horrendous pollution of our northeast rivers and bays. Under my statutory powers to protect the public in an emergency, it was further necessary for this State to commendeer three ocean-going barges and their crews to effect the disposal of sludge-the material removed from sewage by treatment-from six of the State's largest sewage treatment plants. Still further, it was necessary for me to seek, and obtain, through the offices of the President of the United States the use of U.S. Coast Guard tugs to propel these barges to sea for dumping. Our inability or failure to take any one of these steps would have resulted in the release into our rivers and bays of 500 million gallons per day of untreated sewage and industrial wastes. This amounts to about one-half of the wastes treated in all of New Jersey's sewage plants and its raw release is clearly intolerable.

The immediate cause of this emergency was the labor strike of tugboat operators. It seems to me, however, that much larger issues are involved than that of the strike.

In the last fifty years the citizens of New Jersey have invested almost $1 billion in sewage collection and disposal systems for the convenience and water quality protection they would provide. With the aid of our 1969 clean water bond issue we are now launched on another $1 billion construction program for water pollution control. For the operation of a substantial part of these facilities precariously to depend on whether or not there is a tugboat strike, or a strike of barge operators or upon the vagaries of weather affecting ocean-going travel, or upon other such undertainties is wrong and unacceptable. Such brinkmanship is incompatible with our ambitious efforts to eliminate the pollution of our waterways.

In addition, there is the question of the impact upon our marine emvironment of the continued practice of dumping millions of tons of sewage sludge, harbor dredgings and certain chemicals in disposal areas less than twleve miles off the Sandy Hook beach. A study of this impact has been underway for more than a year by the Sandy Hook Marine Laboratory on behalf of the U.S. Army Corps of Engineers. An interim report of the findings of this study was made available to us late yesterday. I have discussed this issue and the significance of the report with officials of the State Health Department.

The report offers evidence that harbor dredgings dumped at the sea disposal site are finding their way to the New Jersey coastline. Evidence has not yet been adduced that sludge dumpings reach our surf waters. It is clear that the disposal sites and their environs are devoid of marine life. I am also informed that the invasion of the red tide-a proliferation of toxic microorganisms- which afflicted our beaches two summers ago may have its genesis in the nutrient materials at the dump site.

While the report deals exclusively with dumping off Sandy Hook, similar questions can be raised about dump sites ten miles from the entrance to Delaware Bay used by the cities of Camden, Philadelphia, Baltimore and others.

All things considered, it is my judgment that the ocean dumping of harbor dredgings and sewage sludge a scant twelve miles from our coast is a primitive, insensitive and unacceptable method of disposal. I realize that as is usually the case in environment protection, there is not a clear choice between the right way and the wrong way. There is a need to make a choice among several somewhat unsatisfactory alternatives. In my opinion we should do the following:

1. Begin phasing out ocean dumping as a regular, accepted method of disposal of sewage sludge off our coast, and of toxic industrial materials off the continental shelf one hundred miles to sea.
2. For the next few years that it will inevitably take to provide on-land sludge disposal facilities require that all dumping of sewage sludge and harbor dredgings be one hundred miles at sea off the continental shelf. This can be accomplished by agreement or by Congressional enactment requiring that such deep sea dumping be a condition of all permits issued by the Army Corps of Engineers.
3. Incorporate in the design of all new sewage treatment plants facilities for sludge disposal other than by dumping at sea.

4. Seek through agreement or by Congressional enactment the requirement by the Army Corps of Engineers that a condition of ocean dumping permits will be a showing by the applicant that some steps are being taken to provide an on-shore treatment and disposal in the future.
5. Seek the agreement of New York State in this changed approach to sludge disposal in recognition of the fact that New York City and other communities now dump more than twice as much sludge as does the State of New Jersey; and, as well, to seek the concurrence of the States of Pennsylvania and Maryland.

I am informed that sludge disposal by landfill or by incineration are not without their own problems-problems of potential land and air pollution, as well as the high cost of facilities. I am also informed that many of the toxic industrial chemicals now disposed of by deep-sea dumping are difficult and expensive to treat otherwise. We hope that in all of these areas technology, upon demand, will give us innovative improvements. In any case, however, hard choices must be made now if we are to restore and protect the quality of our physical environment.

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27 Abstract

This document reports on the "state of the art" of pesticide manufacturing waste treatment and disposal practices. An indepth review of the literature, including government information documents, technical reports, the technical journals, industrial publications and twenty plant interviews with plant managers and operators were used as the data base for this study. The information is presented as concisely and objectively as possible. No attempts were made to prove or disprove statements made in the literature or statements made in the interviews. The report contains chapters dealing with: a) the present and rpojected pesticide demands in the United States, b) the chemistry of pesticides including production processes and waste generation, c) waste treatment possibilities discussed in the literature, d) pesticide waste treatment systems that have been or currently are in full scale operation and, e) the cost of pesticide waste treatment systems. Conclusions and recommendations are presented. Eighty-six references are included in the report.

Abstractor Patrick R. Atkins
Institution University of Texas at Austin

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